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# SOIL SCIENCE

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## Contents

Some Important Soil Profiles of Southern Puerto Rico. JAMES THORP..... 241
A Method for Determining Combined Water and Organic Matter in Soils. GEORGE BOUYOUCOS..... 259
On the Determination of the Ion Exchange Capacity of Soils. J. S. CSIKY.. 269
Some Transformations of Urea and Their Resultant Effects on the Soil. H. W. JONES..... 281
Boron Requirements of Cotton. FRANK M. EATON..... 301
Soluble Aluminum Studies: II. Minimum Concentrations of Aluminum Found to be Toxic to Corn, Sorghum, and Barley in Culture Solutions. W. S. LIGON AND W. H. PIERRE..... 307

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# SOME IMPORTANT SOIL PROFILES OF SOUTHERN PUERTO RICO

JAMES THORP[1]

*U. S. Department of Agriculture, Bureau of Chemistry and Soils*

Received for publication April 8, 1932

The information which appears in the body of this report was obtained in connection with the soil survey of the Ponce area, Puerto Rico, during the winter season of 1929–30.

The accompanying map (fig. 1) of Puerto Rico (10) shows the principal physiographic features of the island, and figure 2 shows in greater detail the physiographic features of the Ponce area.[2] This area, on which the soils were studied in detail, lies largely between Ponce and Salinas and between the Caribbean Sea and the foothills of the main mountain mass of the island. It embraces about 150 square miles. Brief reference is also made to other parts of the island for purposes of comparison.

## CLIMATE

Puerto Rico lies well within the tropical zone and being far removed from large land masses, has a distinctly oceanic climate (2). The trade winds which blow almost constantly from the northeast bring large quantities of moisture, and the upward deflection of these winds by the mountains of the island causes a heavy precipitation on the northern and central parts of the island (fig. 3). As the winds descend toward the south coast they are adiabatically warmed and tend to take up rather than deposit moisture. The Ponce area is then, much drier than the northern and central parts of the island. Great local variations of rainfall in the southern coastal plain are demonstrated by the records for Juana Diaz and Hacienda Potala, which are only 3.4 miles apart. The former receives 51.65 inches and the latter only 28.79 inches. The maximum precipitation for the area is probably about 60 inches and the minimum is probably less than 25 inches.

The average annual temperature of the Ponce area is approximately 78°F. with an annual variation from this average of not more than 1°. The diurnal

[1] The author is especially indebted to Mr. Guillermo A. Torruella for his assistance in the field, and to Director R. Fernandez Garcia and to Mr. Jose H. Ramirez of the Insular Experiment Station, for assistance in the laboratory investigations. Dr. N. L. Britton, of the New York Botanical Gardens and author of many articles and books on the flora of Puerto Rico and elsewhere, made valuable contributions by identifying numerous plant specimens collected in connection with the studies of the solonchak soils.

[2] Thorp, J., and Torruella, G. A. 1930 Soil Survey of Ponce Area. (Unpublished preliminary report to be embodied later in Soil Survey of Porto Rico).

variation is seldom more than 20°. The highest temperature recorded for the island is 100° at Ponce; the lowest recorded is 41° in the high mountains (2).

## VEGETATION

Corresponding to the great variation in rainfall in the Ponce area there is a comparable variation in vegetation. The sandy coast line, where well drained,

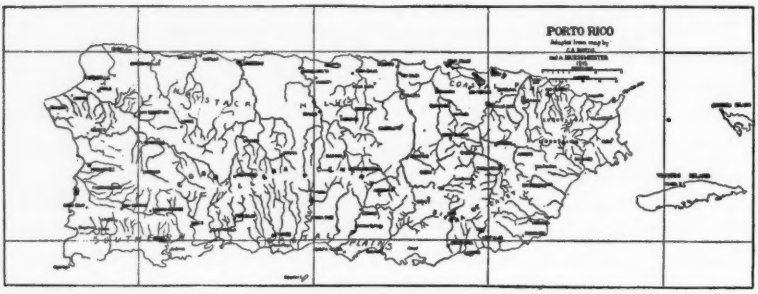


FIG. 1. MAP OF PORTO RICO

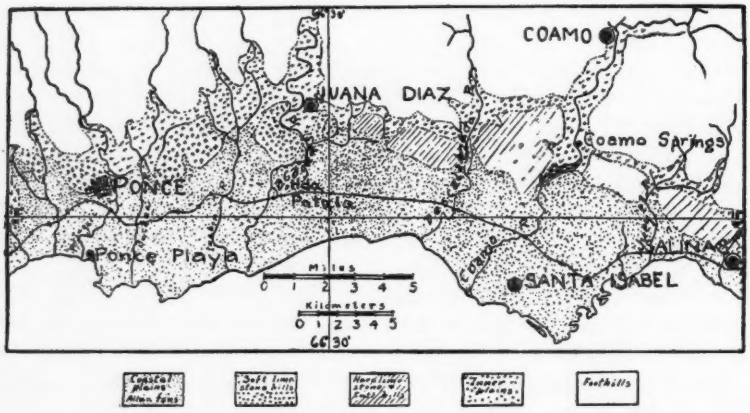


FIG. 2. PHYSIOGRAPHY OF PONCE AREA
(After Lobeck)

supports a xerophytic growth of cactus, chaparral, and grasses. Poorly drained areas near the seacoast (and elsewhere) are likely to contain salts and alkali and when this is the case they support a halophytic type of vegetation. The front range of soft limestone hills is covered by a xerophytic chaparral which has, in places, been cleared and planted to guinea grass for pasture. The coastal and inner plains have been so largely cleared and cultivated that

it is difficult to determine the original type of vegetation. From a few nearly virgin areas observed the normal vegetation of these areas appears to be a combination of xerophytic grasses and a scattering of trees, of which the bucar is one of the most common. These grasses extend well up on the convex slopes of the foothills, whereas mesophytic forest growths cover the moister concave slopes of the adjacent ravines (1).

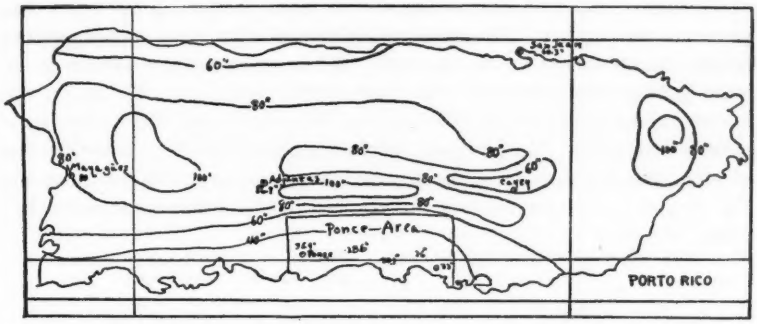


FIG. 3. RAINFALL OF PORTO RICO IN INCHES
(Data from the U. S. Weather Bureau)

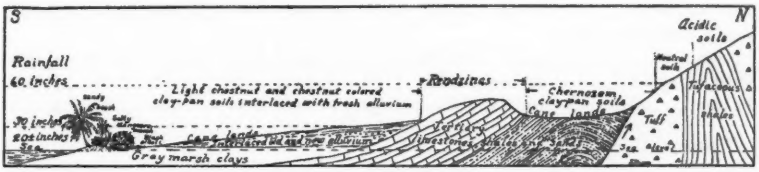


FIG. 4. IDEAL CROSS SECTION IN PONCE AREA NEAR JUANA DIAZ SHOWING RELATIONSHIP OF SOILS TO CLIMATIC AND GEOLOGICAL FACTORS
Not drawn to scale. Geologic section adapted from Mitchell (8)

## SOILS

One of the first questions asked by the average soil investigator is "Did you see any laterites in Puerto Rico?" or, "Are all soils in Puerto Rico lateritic?" We may unreservedly answer "No" to the last question, about which more will be given later. There is a fairly large area of ferruginous laterite on the Mayagüez mesa and at a few other points on the island. Fettke and Hubbard (5) describe the limonite deposits on the Mayagüez mesa as being residual in origin and offer analyses of the deposit and the underlying serpentine as proof. These deposits are described as being practically identical to those found in northeastern Cuba. The deposits in Cuba are described by Marbut (7) as true laterites. Mitchell (8) studied the laterite deposit on Mayagüez mesa

and confirms the opinions of Fettke and Hubbard regarding it. Sweet (11) describes lateritic soils found in the San Juan area and elsewhere in his paper read before the American Soil Survey Association in 1929. Our purpose is to describe a group of tropical soils, which because of climatic differences, are in no way related to the laterites and lateritic soils briefly mentioned in the foregoing.

In mapping the soils of the Ponce area after the usual manner of the Bureau of Chemistry and Soils, approximately 29 series comprising 90 types and phases were separated. This great multiplicity of series, types, and phases can be directly attributed to the complexity of the environmental factors of climate, geology, drainage, and, to a lesser extent, vegetation. The reader will not be interested in the tiresome details of the points upon which these separations were made. We propose, therefore, to describe briefly a few profiles of well-drained mature soils, the general characteristics of the rendzinas and the general conditions existing among the poorly drained and solonchak soils.

TABLE 1

*Base exchange N $NH_4Cl$ of the heaviest layer of four "clay pan" soil types**

| SOIL TYPE | DEPTH | S. S. NUMBER | LABORATORY NUMBER | $R_2O_3$ | CaO | MgO | $K_2O$ | $Na_2O$ |
|---|---|---|---|---|---|---|---|---|
| | *inches* | | | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* |
| Ponceña clay | 12–16 | 580502 | 8107 | 0.0000 | 1.32 | 0.055 | 0.013 | 0.020 |
| Santa Isabel silty clay loam | 6–12 | 580526 | 8108 | 0.0025 | 0.94 | 0.064 | 0.009 | 0.080 |
| Paso Seco loam | 16–28 | 580570 | 8109 | 0.0000 | 0.68 | 0.075 | 0.010 | 0.016 |
| Fe clay | 10–22 | 580558 | 8110 | 0.0000 | 0.97 | 0.074 | 0.016 | 0.022 |

* Analyst G. Edgington, August 12, 1931.

Since all of the maturely weathered soils of the Ponce area have most of the morphological characteristics of the true solonetz type, one may say that a normal or zonal profile is non-existent there. Base exchange investigations (table 1) indicate that from a chemical standpoint, as interpreted by the Russian soil scientists, these soils cannot be classed as true solonetz. In order to avoid confusion, therefore, we shall refer to them as "clay pan" soils.

There are at least two types of these "clay pan" soils corresponding to climatic differences. One of these is the chernozem-"clay pan" soil and the other is the chesnut-colored "clay pan" soil. The former occurs under a rainfall of from approximately 40 inches to approximately 60 inches. The chestnut-colored "clay pan" soil occurs under rainfalls varying from about 25 inches to about 40 inches. Possibly one might find a few areas of light chestnut-colored "clay pan" soil in the Ponce area. Opinions differ so widely on colors and degrees of darkness of color that we hesitate to make positive statements.

*Profile 1*

Profile 1 was taken from the unplowed margin of a smooth, gently sloping cane field 1 kilometer northwest of Coto Laurel. This field lies on the inner plains between the range of limestone hills and the foothills of the mountains. It receives an annual precipitation of 45 to 50 inches. Virgin areas are very small and are covered chiefly by pasture grasses with a scattering of various kinds of trees. A description follows:

| HORIZON DEPTH *inches* | HORIZON DESCRIPTION |
|---|---|
| 0–12 | Very dark brown to black clay. Highly granular, the grains being fine near the surface and gradually increasing in size with depth. Very plastic when wet. No effervescence with HCl. Many coarse and fine roots. |
| 12–16 | Dark brown, *very heavy* and *tough* clay mottled with black clay from above horizon. It is the heaviest layer of the profile and forms large, very hard columnar clods when dry. No effervescence with acid. Roots less abundant than in the above horizon. |
| 16–26 | Yellowish brown, *heavy* and *tough*, roughly columnar clay with black soil from the surface horizon in irregular vertical tongues following the soil cracks. No effervescence. A few roots. |
| 26–30 | Light yellow-brown silty clay with a few white, soft lime concretions. Interstitial soil effervesces with acid. |
| 30–54 | Yellow-brown silty clay mottled brown, red, yellow, and white. The latter is due to lime, which is in one-fourth to one-half inch concretions, soft on the outside and hard in the middle. This is the horizon of maximum lime accumulation. There are many roots. |
| 54–66 | Shaly limestone (or limy shale) mottled yellow, reddish yellow, and gray. Effervesces freely with acid. Texture, silty clay loam. This is the parent material and it shows distinct lines of stratification. It seems to have much less lime than the horizon above it. |

Since the first profile, described to represent the chernozem-"clay pan", is derived from a shaly limestone it was thought best to describe another soil of the same group in order to prove that the dark color of the soil and the accumulation of the lime are not due simply to the nature of the parent rock. For this purpose a soil of another series is described in the following. This was taken from a high alluvial terrace about 3 kilometers east of Juana Diaz plaza and just north of the Military Road. The alluvial materials consisted of tufaceous shale fragments, basic igneous gravels, and occasional hard limestone fragments. It will be noted that this soil differs in broad characteristics from profile 1 in having its lime accumulation at a greater depth.

*Profile 2*

| DEPTH *inches* | DESCRIPTIONS OF HORIZONS |
|---|---|
| 0–2½ | Dark gray-brown, very fine granular silty clay, matted with grass roots. |
| 2½–10 | Dark gray-brown clay, nearly black when wet. Forms large granules and small clods which subdivide with difficulty into a medium granular structure. Many areas of this soil are practically black in this horizon. |
| 10–18 | Very heavy, tough, cloddy, roughly columnar brown clay. Heaviest horizon of |

profile. There are some angular gravels, many grass roots in the cracks, and many vertically distributed dark-colored soil deposits in worm holes.

18–30 Light brown clay loam, heavy, porous, and cloddy. Much angular gravel. No effervesence with acid.

30–42 Same as above with a slight effervescence with acid and with a larger proportion of gravel.

42–60 Interstratified layers of gravel, sand, and silty lime deposits, the latter strongly predominating.

60–72 Loose stratified gravel and sand. Little lime present.

In many places this profile is underlain by a series of buried soil profiles, each with its horizon of lime accumulation. The predominate color of these buried soils is reddish or purplish. Profile 2 supports a xerophytic vegetation, chiefly grasses.

Nearly all of the chernozem-"clay pan" soils are on the inner plains. The chestnut-colored "clay pan" soils lie chiefly on the broad alluvial fans which make up a large part of the coastal plains. There are several series of these soils, but a description of one or two will suffice.

*Profile 3*

| DEPTH *inches* | DESCRIPTIONS OF HORIZONS |
|---|---|
| 0–6 | Dark brown, coarsely granular silty clay loam, turning light brown when crushed. |
| 6–12 | Dark brown (lighter colored when crushed), very heavy and tough silty clay. Contains a few angular lime concretions but the interstitial soil does not effervesce. |
| 12–18 | Brown silty clay loam full of hard angular lime concretions and worm holes filled with dark brown material from above. Slightly compact. |
| 18–36 | Alternating layers of yellowish brown fine sandy loam and silt loam with many spots of soft lime, some small iron rust stains, and some gray mottling. Iron streaks are very abundant at the bottom, in some places forming a hardpan. |
| 36–40 | Yellow-brown fine sandy loam to loamy sand with some gray and rusty mottlings and occasional limy spots. Often this layer does not effervesce with acid. |

Profile 3 was taken from the edge of a cane field on the seacoast $2\frac{1}{4}$ kilometers west of Pastillo. The A horizon has been somewhat disturbed by plowing operations. Different members of this series show considerable variation in the thicknesses of the different horizons.

Another "clay pan" profile which occurs in fairly large areas of the coastal plain lacks the usual horizon of lime accumulation. It seems probable that this may be due to lack of sufficient bases in the parent materials to cause the formation of lime. The chief parent material seems to be quartz sands. It may also be possible that the more porous nature of the soil has permitted leaching to extend to a greater depth. A sample of this soil, taken from a high alluvial terrace just northeast of Barrio Paso Seco, is described in the following.

*Profile 4*

| DEPTH *inches* | DESCRIPTION OF HORIZONS |
|---|---|
| 0–8 | Dark brown loam, coarsely granular, with granules which break up fairly easily into single grains. |

8–16 Dark brown (yellow-brown when crushed) silty clay loam, coarsely granular to finely cloddy.

16–28 Heavy, brown, *very tough* silty clay, columnar in form. There are many insect burrows filled with dark-colored organic material from above. The soil is yellow-brown when crushed.

28–44 Light brownish yellow, cloddy, somewhat tough loam to fine sandy loam. Columnar form. There is some dark-colored material in the worm holes.

44–60 plus Light brownish yellow loamy fine sand; structureless.

This sample came from a road cut and was in a semi-virgin condition. Grass roots were especially abundant in the two upper horizons. Natural vegetation on this type is xerophytic.

Another soil with a very similar structural profile, but having a nearly black A horizon was found to have unsymmetrical lime concretions about 1 inch long and ½ inch thick between the depths of 4 and 5 feet. These concretions appeared to have been partly dissolved and there was no interstitial lime in the soil. This sample was observed on a high terrace in the southwestern edge of the city of Juana Diaz.

Mature soils of the Ponce area have the following striking characteristics in common:

A thick (10 inches–15 inches), heavy textured (with few exceptions), granular A horizon, gray-brown to nearly black in color, according to climatic conditions.

An extremely heavy, columnar, prismatic, or blocky B horizon containing vertical streamers of dark-colored material washed in from the A horizon.

A horizon of lime accumulation (with the exception of one series), the lime occurring both in concretions and in the silty or crypto-crystalline forms.

With the exception of profile 1, and a very few others not here described, the mature soils are derived from old alluvial fan and high terrace deposits of varying composition.

In a few areas near the soft limestone hills, notably near Central Mercedita, there are a few rendzina-like soils. Their A horizons range in color from brown to black. They can scarcely be classified as true rendzinas because there is usually a feeble development of the heavy B layer which characterizes the "clay pan" soils. This development is never very pronounced, however. These soils are underlain by either a soft chalky limestone or by alluvial material consisting entirely of outwash from the soft limestone hills. In places where the outwash from the soft limestone hills is mixed with material from the igneous rocks of the interior, the profile more nearly approaches the true "clay pan" type.

The poorly drained soils of southern Puerto Rico are derived mainly from lagoon and estuarine deposits which lie at or very near sea level. The soils of both the old and recently deposited alluvial fans abut on these filled-in lagoons and estuaries and are poorly drained near the line of contact. In the virgin condition these soils range from pale gray to nearly black at the surface and all of them except a few areas of peat and muck have predominately gray subsoils. In a few places lime concretions similar to those described in

profile 3 of the mature soils are encountered at depths of from 1 to 3 feet. These concretions seem to represent the average position of the water table. With the exception of peat and muck most of the poorly drained soils contain lime from the surface downward. It is usually in the form of sea shell fragments. In the poorly drained soils the water table is encountered from the surface to depths of 5 or 6 feet. Some places are marshy at all times whereas at others there may be water at the surface part of the time with the true water table lying at 30 inches or more.

Some of the best cane soils of the south coast are those which are of recent alluvial origin (3). Their lack of definite profile characteristics makes them uninteresting from a purely scientific viewpoint. They lie on the same alluvial fans as some of the mature soils, and, because the river courses sometimes change, these soils often interlace with those showing mature development. Most of these soils will effervesce with dilute HCl from the surface downward because of the inclusion of quantities of ground-up land-snail shell fragments. These shells are also frequently found in the A horizons of the mature soils.

A common characteristic of all the soils of the region, excepting those which are swampy or heavily impregnated with salts, is brought about by the very great activity of earthworms and burrowing insects, especially the former. Myriads of deposits brought from the deep subsoils are deposited in the upper horizons and great quantities of material are also carried down from the surface to the B and C horizons. This activity of the earthworms is greater than we have ever observed in any other group of soils.

Land crabs are very active in the poorly drained soils. They burrow from the water table to the surface and build chimneys of gray mud on the surface like those of the crawfish in the Southern States. They are sometimes a serious pest in the cane fields and are systematically poisoned (3).

Determinations of pH values made by the LaMotte colorimetric method indicate that nearly all of the soils of the Ponce area react well above pH 7.0 in the surface and well above 8 in the lower B horizon. The soils of the coastal plain, peat and muck excepted, usually react above pH 8.0 at the surface.

In local spots scattered over the coastal and inner plains the pH has been considerably raised by thick deposits of seashells mixed with wood ashes and broken pottery fragments. These places are the old camping grounds of the aborginees and are known as "kitchen middens." Many very interesting implements have been found in these places.

### *Solonchak soils*

The solonchak soils, or those containing large quantities of salts, may be grouped into two or more classes according to the relative proportions of sodium carbonate to the other soluble salts. In making a map of these soils for the

use of the experiment station, 16 classes were separated. These separations were based on the percentage of total salts as determined in the field by the electrolytic bridge and the approximate ratios of sodium carbonate to other salts as determined by the strength of color produced with phenolphthalein. Obviously the latter test cannot be considered as quantitative. The information obtained is shown in table 2.

Salt crusts were collected from different localities and analyses for the ions indicated in table 3 were made. The following methods of analysis were used in determining the ions:

$Na^+$,—zinc uranyl-acetate
$Mg^{++}$ and $SO^{--}_4$—gravimetric method
Remainder by volumetric method

TABLE 2

*Field tests on 198 4-foot alkali soil samples*

| | REACTION WITH PHENOLPHTHALEIN* | | | | |
|---|---|---|---|---|---|
| | Red | Pink | Pale Pink | No color | Totals |
| Reaction with phenolphthalein increases downward, indicating downward proportional increase in $Na_2CO_3$ in relation to other salts | 10 | 13 | 35 | 0 | 58 |
| Reaction with phenolphthalein decreases downward, indicating conditions opposite to above | 20 | 14 | 13 | 0 | 47 |
| Percentage of total salts increases downward | 0 | 9 | 19 | 23 | 51 |
| Percentage of total salts decreases downward | 39 | 22 | 40 | 46 | 147 |
| Percentage of total salts to dry soil for entire 4-foot profile: | | | | | |
| Less than 0.2 per cent | 0 | 1 | 8 | 20 | 29 |
| 0.2–0.4 per cent | 1 | 6 | 12 | 22 | 41 |
| 0.4–0.6 per cent | 11 | 14 | 8 | 6 | 39 |
| 0.6–1.0 per cent | 13 | 6 | 12 | 8 | 39 |
| 1.0–3.0 per cent (and over) | 14 | 4 | 19 | 13 | 50 |

* Numbers indicate the number of 4-foot samples in each category.

Although the results of the analyses of samples II, V, VII, and VIII do not agree well with the totals yet they will serve in a general way to show the approximate proportions of the different water-soluble salts.

Samples I and VI are "white alkali" with sodium chloride predominating and with just a little carbonate and bicarbonate in each. Sample II is an excellent example of a balanced "white alkali" in which all of the common "white alkali" salts are present, but in which sodium carbonate is lacking. In samples III, V, and VII, "white alkali "predominates but there are appreciable quantities of "black alkali." Samples IV and VIII are typical "black alkalis," with large quantities of sodium carbonate present.

There are several sources which contribute to the supply of soluble salts which occur in the solonchak soils of this region. The alluvial fans have been gradually encroaching on the Caribbean Sea and its various lagoons and estuaries. All of these bodies of water are more or less salty or brackish, the principal salt being NaCl. Some of the limy shales, such as those from which soil profile 1 is derived, carry considerable quantities of gypsum. Crystals of this salt were found in a fresh cut which was being made through a hill for the accommodation of an irrigation ditch. In the same place a small flow of water was encountered which contained nearly 2 per cent NaCl. Sodium carbonate and calcium chloride may be produced by the reaction of calcium

TABLE 3

*Chemical analysis of alkali crusts from salty soils, Ponce Area**

| NO. AND LOCATION OF SOIL SAMPLE | I<br>0.4 KM. EAST OF PLAYA ON CENTRAL CONSTANCIA ROAD | II<br>0.4 KM. NORTH OF PASTILLO ON URSULA ROAD | III<br>0.4 KM. EAST OF PASTILLO | IV<br>1.4 KM. SOUTH OF HCDA. ESPERANZA PLAZA | V<br>1.2 KM. SOUTH ON ROAD BETWEEN LOS PAMPANOS AND THE PLAYA CEMETRY | VI<br>JUST WEST OF MERCEDITA GATE | VII<br>JUST WEST OF RIO PORTUGUÉS AT PLAYA PONCE | VIII<br>SALTY SOIL NEAR GATE TO HCDA. SERRANO |
|---|---|---|---|---|---|---|---|---|
| | *p.p.m.* | *p.p.m.* | *p.p.m.* | *p.p.m.* | *p.p.m.* | *p.p.m.* | *p.p.m.* | *p.p.m.* |
| Total solids | 65,615 | 17,980 | 6,548 | 23,480 | 14,089 | 158,379 | 93,312 | 7,946 |
| Lost on ignition | ..... | 3,499 | 1,198 | 2,163 | 2,958 | ..... | ..... | 1,564 |
| Calcium | 161 | 824 | 96 | 101 | 87 | 1,794 | 3,555 | 70 |
| Sodium | 24,253 | 3,535 | 1,632 | 5,106 | 5,145 | 58,680 | 20,175 | 2,623 |
| Magnesium | 148 | 477 | ..... | ..... | 56.0 | 2,601 | 4,190 | 37.0 |
| Carbonates | 51.4 | ..... | 100 | 3,040 | 525 | 76 | 103 | 2,400 |
| Bicarbonates | 317.0 | 322 | 580 | 2,542 | 1,293 | 583 | 247 | 1,923 |
| Chlorides | 37,639 | 5,725 | 1,861 | 5,096 | 1,623 | 65,007 | 42,106 | 533.0 |
| Sulfates | 1,784 | 1,491 | 898 | 5,106 | 7,334 | 24,428 | 5,174 | 653 |

* Analyses by Mr. Jose H. Ramirez, chemist, Insular Experiment Station.

bicarbonate and sodium chloride (4). Some authors, however, question whether this reaction takes place in the soil (6). This fact was noted in the field at any rate: Excess NaCl and $Na_2SO_4$ are present in the moist soils adjacent to the aforementioned lagoons and estuaries, and $Na_2CO_3$ is of common occurrence where these poorly drained salty soils come into contact with those containing more or less calcium carbonate.

The 198 4-foot alkali samples[3] shown in table 3 bring out the following points of interest:

[3] These samples were taken during the dry season when efflorescences were common on the surfaces of the alkali soils.

Sufficient color with phenolphthalein to indicate the presence of appreciable quantities of $Na_2CO_3$ (or $K_2CO_3$) was shown by 65.2 per cent of all samples taken. A medium to strong reaction with phenolphthalein was shown by 30.3 per cent of all samples.

When the ratio of sodium carbonate to other salts is low the former is more concentrated in the subsoil than at the surface.

Vice versa, when the proportion of sodium carbonate is high it tends to concentrate in the surface horizon.

There is a general tendency for all salts to be more concentrated in the surface horizon than in the subsoil.

A study was begun of the principal halophytic plants in relation to the percentage and kinds of salts in the alkali areas. This material is presented in brief form in the following.[4]

Two of the most satisfactory alkali indicators are the verdolaga rosada (*Sesuvium portulacastrum*) and the barilla (*Batis maratima*). The former is most commonly found on soils containing from 0.6 per cent to 3.0 per cent total salts of which only a small proportion is sodium carbonate. It also grows on white alkali soils where the total salts exceed 1.0 per cent. It is occasionally found on soils having a low percentage of salts most of which is sodium carbonate. The barilla is confined almost entirely to areas where the salts are chiefly of the "white alkali" variety (mostly NaCl) and where the percentage is between 0.6 and 3.0.

Sedges (*Fimbristylis*) are practically always on soils which are moderately salty. Their presence is dependent largely on having very moist soil which, a large part of the time, is actually wet. The eneas or cattails (*Typha angustifolia*) grow in marshy places. There is usually less than 0.4 per cent salts where the eneas grow in abundance. Mangles or mangroves of several species grow in marshy soils near the sea and in semi-marshy flats associated with barilla. They are commonest where the ratio of sodium carbonate to other salts is low, but they will flourish in any wet alkali soil where the salt percentages range between 0.2 and 3.0. The matojo de playa (*Sporobolus virginicus*) usually grows in salty soils near the sea. It will tolerate a high percentage of salts but is not common on black alkali soils. *Jaquemontia subsalina* and *Evolvulus glaber* are good salt indicators but are not easily noticeable. They are both small creeping vines with pale blue flowers. They occur on alkali soils where the ratio of sodium carbonate to white alkali is small and where the total salts range from 0.4 per cent to about 2.0 per cent. These last figures are from rather meager data. The cotorrera de playa (*Heliotropium curassavicum*) is fairly common on all grades of alkali land except those where the salt percentage is very high.

One of the commonest plants on the alkali soils of the Ponce area is the grass known as horquetillo (*Chloris radiata*). It grows on all grades of alkali soil

[4] We are indebted to Dr. N. L. Britton of the New York Botanical Gardens for identifications of plants.

but cannot be used as a sure indicator because it also flourishes on non-alkali soils. There are many other plants, such as various cacti, shrubs, and trees, which fall into the same category.

A poor grade of sugar cane was observed growing on soils where the percentage of alkali runs as high as 0.6 per cent. Where the alkali is of the white variety the cane shows little damage under percentages up to 0.4 per cent but noticeable damage from black alkali occurs with 0.2 per cent or less.

## SUMMARY

Soils discussed in this paper are found in south central Puerto Rico where the climate is warm and comparatively dry. The average annual temperature is 78° and the annual precipitation varies from 25 to 60 inches. As a result of the high annual evaporation the mature soils of the region belong to the chernozem and chestnut-colored soil groups. The normal profiles for these soils are not developed but take the form of chernozem-"clay pans" and chestnut-colored "clay pans"

Where the alluvial fans of the coastal plain approach the marshy lands and lagoons bordering the Caribbean Sea, alkali and soluble salts have accumulated in many of the soils to such an extent as to retard or prevent agricultural pursuits. These "alkali spots" support a typical halophytic vegetation.

All soils of the area, except peat and muck, so far as observed, have pH values well over 7.0, many of them exceeding 8.0 Worms and insects have accomplished much in the translocation of soil materials from one horizon to another in all of the soils except those which are very salty or very wet. In the latter the land crabs are very active in transferring material from the subsoil to the surface.

A list of the principal halophytic plants and the types of salty lands to which they are adapted is given.

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## PLATE 1

SOILS OF PUERTO RICO

FIG. 1. Note the coarsely granular surface soil, the exceedingly heavy and cloddy upper subsoil, and the white silty and concretionary line accumulations.

FIG. 2. A chernozem-clay pan soil just west of Coamo Springs. Note the white, soft lime concretions above and silty lime below; also the prismatic structure to the left of the pick. Surface not shown.

FIG. 3. Hard limestone hill southwest of Coamo Springs. Soils are rendzinas. River terrace in foreground.

FIG. 1

FIG. 2

FIG. 3

PLATE 2

VEGETATION ON PUERTO RICO SOILS

FIG. 1. Heavy sugar cane yield on recent alluvial soils near Hacienda Cortada. This field produced 75 tons an acre in the spring of 1930. *Gran cultura* crop.

FIG. 2. A study of halophytic vegetation near the south coast of Puerto Rico. Mangroves in left background. Colony of barilla in foreground. Verdolaga rosada (*Sesuvium*) just to left of figure. Matojo de playa between figure and right background. White patches are crystallized soluble salts.

FIG. 1

FIG. 2

# A METHOD FOR DETERMINING COMBINED WATER AND ORGANIC MATTER IN SOILS[1]

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Combined water in soils presents a problem of the most important and fundamental nature because of the rôle it plays in their mechanical and chemical analyses and in the determination of their organic matter. By combined water, is meant that water which remains in soils after they have been dried at a temperature of 108°C. for 24 hours. It may be water of crystallization, constitution, or imbibition, or combinations of these. Although its existence in soils and its importance are generally recognized, there is at present no method for its direct determination.

In the course of study of soil moisture at this laboratory (1–6), the idea occurred to the writer that the combined water in soils might be directly determined by means of distillation at a high temperature. It seemed possible that if this method succeeded, then the ignition method for determining organic matter would become more accurate and dependable, since the great source of error in this method is the uncertainty concerning the quantity of combined water present in soils.

Happily, the idea and principle of determining the combined water by the distillation method seem to be sound and successful and, because of this success, the ignition method for determining organic matter in soils becomes more accurate and reliable. In addition, the distillation method can also be used to determine the total water content in soils. This latter subject, however, will be considered in a subsequent paper. Although the method seems to have proved successful and has given definite results, yet this report should be considered as preliminary to a more complete investigation. The investigation of the whole subject is being continued with special effort to perfect further the technique and apparatus.

## METHOD AND PROCEDURE

The distillation apparatus employed for determining the combined water in soils is shown in plate 1. It consists of a 250-cc. bomb made of iron pipe. The cap is screwed on. In a hole in the center of the cap is brazed a short

[1] Journal Article No. 103 (U. S.) from the Michigan Agricultural Experiment Station.

[2] The chronological order of publication of this paper and that of one by the same author, dated March 21, are reversed at the author's request.

½-inch pipe and to this pipe is brazed a copper tube ⅛ inch inside diameter and 2 feet long. This copper tube is passed through a condenser made of lead pipe soldered near the center of the copper tube. The condenser can be either connected to a faucet with running water or kept filled with cold water. The combined water is caught in a special very narrow cylinder graduated to 0.1 cc. and containing carbon tetrachloride. The carbon tetrachloride is essential because it dissolves or coagulates any organic matter that may be distilled over and greatly facilitates the accuracy of reading the water column in the cylinder.

The procedure for determining the combined water consists of first preparing the soil by passing it through a 2-mm. sieve then testing it for carbonates. If carbonates are present they are destroyed with hydrochloric acid and then the soil is thoroughly washed, dried, and screened again. Soils that have no carbonates are not treated with the acid. Exactly 100 gm. of the air-dry soil is then placed in the bomb and about 30 gm. in a crucible. The latter sample is used to determine the hygroscopic moisture and the ignition loss of the soil.

TABLE 1

*Tests of the degree of accuracy of the distillation method*

| SOILS | WATER ADDED | WATER RECOVERED |
|---|---|---|
| | *cc.* | *cc.* |
| Quartz sand, dried | 10.00 | 10.00 |
| Davidson loam, ignited | 10.00 | 9.90 |
| Ontonogan clay, ignited | 10.00 | 10.00 |
| Fargo clay loam, ignited | 10.00 | 9.90 |
| McKenzie clay, ignited | 10.00 | 9.90 |

The lid is screwed on the bomb and the joints are covered with a layer of asbestos cement to make sure that the bomb is air-tight. The process of putting on and taking off this asbestos cement is very simple and does not take more than two minutes. The bomb is now placed in the electric muffle, the cylinder containing the carbon tetrachloride is connected to the end of the copper tube, and the condenser is connected to the faucet. The current is turned on and regulated to produce a temperature of 800°C. in the case of mineral soils and about 330°C. in the case of peats and mucks. The water distills very rapidly and rises to the top of the carbon tetrachloride. It is very clear except in peats, in mucks, and in mineral soils containing an extremely large amount of organic matter, in which cases it is slightly brown. There may also be a thin layer of coagulated organic matter between the water and carbon tetrachloride in case of some of the organic soils but the error that may arise from it is negligible. The water standing above the column of carbon tetrachloride represents both the hygroscopic and combined water of the soil and its volume is read and recorded. When distillation is complete the bomb is replaced in the muffle by another one containing a different soil. By having a

set of three or four bombs, which can be easily made at a machine shop for about $2 each, and by maintaining the temperature of the muffle at 800°C., the combined water of three or four soils can be determined in about one hour. It was experimentally found that if a soil is placed in a furnace at a temperature of 800°C. no more water is distilled from it after 15 minutes.

Before the method was employed to obtain final experimental results its degree of accuracy was tested by adding a definite amount of water to dried quartz sand and to ignited soils having no hygroscopic or combined water, and then recovering the water added. Before this was done, however, the attraction of the copper tube for a film of water was satisfied by running one or two preliminary experiments. The results obtained are shown in table 1.

It is seen that the quantity of water recovered in each case agrees quite satisfactorily with the quantity added.

The two great sources of error in the method lie in not having the cap on the bomb air-tight and in the danger of some soil getting into the copper tube and thus either preventing the distillation or absorbing some of the water that is being distilled. The first danger is completely eliminated by covering the joint between the cap and the bomb with asbestos cement. The second danger can be easily avoided by care in handling the bomb after the soil is placed in it. The copper tube should also be frequently cleaned with alcohol and water. It is advisable to use a separate bomb for the organic soils.

## EXPERIMENT RESULTS

In table 2 are presented the experimental results as obtained by the distillation method on the combined water and organic matter in soils. The combined water is the difference between the hygroscopic water lost at the temperature of 108°C. for 24 hours and the total water distilled from the air-dry soil. The ignition loss was obtained in the electric muffler at the temperature of 800°C.—the same as that used for distillation—on soils previously dried at 108°C. for 24 hours. The organic matter is obtained by subtracting the combined water from the total ignition loss. No correction is made for carbonates, since they were destroyed by the acid treatment.

The results in table 2 show that the combined water varies greatly in the different soils.

The results on combined water and ignition loss of the first 11 soils present the real test as to the soundness, accuracy, and reliability of the distillation method for determining combined water in soils. These first 11 soils and artificial materials, as far as could be ascertained, contain no organic matter or carbonates. Provided that the loss on ignition is due to combined water alone, then the combined water as obtained by the distillation method should equal the loss on ignition. That is exactly what takes place. It will be seen that the figures for combined water and ignition loss for all of these 11 soils and artificial materials, are remarkably close. This close agreement is significant and should be considered as affording a real test for the method.

When the soils containing organic matter are examined, however, it is seen that the figures for combined water and ignition loss are far from being in close

TABLE 2

*Combined water as obtained by the distillation method, and organic matter determined indirectly by calculating the difference between combined water and ignition loss*

Soils 1 to 11 contained no organic matter or carbonates

| SOILS | $CaCO_3$ | HYGROSCOPIC MOISTURE AT 108°C. | LOSS ON IGNITION FROM SOILS DRIED AT 108°C. | COMBINED WATER DISTILLED OVER FROM SOILS DRIED AT 108°C. | ORGANIC MATTER CORRECTED FOR CARBONATES AND COMBINED WATER |
|---|---|---|---|---|---|
| | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* |
| 1. Silica gel | 0 | 3.79 | 2.92 | 3.02 | |
| 2. Bentonite | 0 | 5.64 | 2.56 | 2.59 | |
| 3. Susquehanna clay, 16–20 inches | 0 | 2.73 | 6.78 | 6.68 | |
| 4. Davidson clay loam, 24–30 inches | 0 | 1.71 | 8.18 | 8.20 | |
| 5. Nype clay | 0 | 2.48 | 10.67 | 11.22 | |
| 6. Parson silt loam, B horizon | 0 | 2.16 | 6.06 | 6.88 | |
| 7. Decatur clay, 6–12 inches | 0 | 1.48 | 4.78 | 4.68 | |
| 8. Iredell loam, 12–16 inches | 0 | 4.18 | 8.70 | 9.42 | |
| 9. Bladen loam, 12–8 inches | 0 | 1.87 | 5.25 | 5.66 | |
| 10. Antinoch clay loam, 40–60 inches | 0 | 2.97 | 2.92 | 2.86 | |
| 11. Greenville fine sandy loam 12–18 inches | 0 | 1.20 | 4.74 | 4.18 | |
| 12. Capay clay | 2.20 | 4.12 | 4.47 | 4.22 | |
| 13. Black clay adobe | 0 | 6.06 | 8.30 | 5.84 | 2.46 |
| 14. McKenzie clay | 0 | 4.40 | 10.00 | 4.65 | 5.35 |
| 15. Clarion silt loam, surface | 0 | 2.59 | 6.18 | 2.67 | 3.51 |
| 16. Houston black clay, 1–12 inches | 24.90 | 2.20 | 8.33 | 3.63 | 4.70 |
| 17. Fargo clay, surface | 0 | 5.90 | 11.70 | 5.90 | 5.80 |
| 18. Fulton clay, subsoil | 15.80 | 2.02 | 4.50 | 3.98 | |
| 19. Haldemond clay, subsoil | 0 | 2.85 | 8.91 | 3.99 | 4.92 |
| 20. Ontonagon clay, C horizon | 28.40 | 1.43 | 3.01 | 2.31 | |
| 21. Lake Charles clay, surface | 0 | 3.43 | 5.42 | 2.95 | 2.47 |
| 22. Clyde clay, surface | 0 | 4.95 | 17.30 | 8.40 | 8.50 |
| 23. Lindly sandy loam, surface | 0 | 1.57 | 4.82 | 2.38 | 2.44 |
| 24. Davidson loam, surface | 0 | 1.72 | 9.60 | 5.58 | 4.02 |
| 25. Clinton silt loam, surface | 0 | 1.43 | 5.10 | 1.97 | 3.13 |
| 26. Putnam silt loam, surface | 0 | 1.88 | 6.33 | 2.40 | 3.93 |
| 27. Barnes loam, subsoil | 15.90 | 2.04 | 3.20 | 2.98 | |
| 28. Muck 1 | 0 | 18.20 | 79.80 | 9.5 | |
| 29. Muck 2 | 0 | 10.00 | 73.20 | 10.4 | |
| 30. Raw peat | 0 | 18.10 | 94.2 | 11.0 | |

agreement. This disagreement is, of course, due mainly, if not wholly, to organic matter, which is present in considerable amounts in some soils, as revealed in the last column of the table.

Since the differences between the ignition loss and combined water amount to about 0.5 per cent in soils that are not supposed to contain organic matter, any differences much less than 1 per cent have probably no significance as far as organic matter content is concerned.

It was feared at the outset that the distillation method might fail in peats and mucks and in mineral soils containing much organic matter because of the possibility that in the destructive distillation of organic matter some water might be formed. Though it is a fact that some plant materials, such as wheat flour, will form water on destructive distillation, no positive evidence is indicated in the aforementioned experimental results that the peats, mucks, and mineral soils with organic matter form water on destructive distillation. This conclusion is based principally on the comparatively small amount of combined water obtained from these organic materials. For instance, in muck 1, muck 2, and in the peat, the percentages of combined water are 9.5 10.4, and 11.0, respectively, and in Clyde clay, which contains 8.5 per cent organic matter, it is 8.40 per cent. In contrast, the combined water in Davidson loam, Nype clay, and Iredell loam, which contain no organic matter, is 8.20, 11.22, and 9.42 per cent respectively. Even if there is a tendency for organic matter to form water upon destructive distillation, the amount would be very small in mineral soils considering their small content of organic matter.

It has already been stated that the temperature used for distilling combined water from peats and mucks is about 330°C., whereas for the mineral soils it is 800°C. The lower temperature for peats and mucks is used because at the higher temperature so much organic matter is distilled over that it is very difficult to measure accurately the combined water. At the temperature of 330°C. very little, if any, organic matter is distilled over, and the water distilled is practically clear and can be measured very accurately.

The point may be raised that if a temperature of 800°C. is required to distill the combined water from the mineral soils, then the temperature of 330°C. may not be sufficiently high to distil all of the combined water from the peats and mucks. It must be stated that even when the higher temperature was used on the peats and mucks it seemed that no more combined water was obtained than at the lower temperature. In fact, the impression has been gained from the various experiments performed that organic matter gives up its combined water with comparative ease and does not require anywhere near as high a temperature as some of the mineral constituents to free it of combined water. Furthermore, it does not seem reasonable that organic matter will fail to give up its combined water at the temperature of 330°C. when it itself begins to break down and distil over at this temperature.

### *Relationship between combined water and clay content of soils*

A comparison of the relationship between the combined water and clay content of soils is shown in table 3. It is evident from this comparison that

though there is a general tendency for the combined water to vary with the clay content of soils, yet there are several soils in which the relationship is not at all close. This is probably as should be expected because not only clay content but also chemical composition should affect the amount of combined water.

TABLE 3

*Comparison between combined water and clay content of soils*

| | COMBINED WATER | CLAY (.005–0 MM.) | FINE CLAY (.002–0 MM.) |
|---|---|---|---|
| | *per cent* | *per cent* | *per cent* |
| Susquehanna clay, 10–20 inches | 6.68 | 41.0 | 39.5 |
| Davidson clay loam, 24–30 inches | 8.20 | 71.2 | 69.1 |
| Nype clay | 11.22 | | |
| Parsons silt loam, B horizon | 6.88 | 64.3 | 60.1 |
| Decatur clay, 6–12 inches | 4.68 | 42.3 | 40.7 |
| Iredell loam, 12–16 inches | 9.42 | 74.1 | 70.4 |
| Bladen loam, 12–18 inches | 5.66 | 54.0 | 48.8 |
| Capay clay adobe | 4.22 | 63.2 | 56.9 |
| Antinoch clay loam, 40–60 inches | 2.86 | 34.8 | 32.4 |
| Greenville fine sandy loam, 12–18 inches | 4.18 | 39.6 | 37.5 |
| Black clay adobe | 5.84 | 55.9 | 52.7 |
| McKenzie clay | 4.65 | 76.1 | 71.9 |
| Clarion silt loam, surface | 2.67 | 24.3 | 21.8 |
| Houston black clay, 1–12 inches | 3.60 | 57.2 | 52.8 |
| Fargo clay, surface | 5.90 | 60.4 | 55.1 |
| Fulton clay, subsoil | 3.98 | 68.0 | 66.5 |
| Holademond clay, surface | 3.99 | 85.6 | 77.4 |
| Ontonagon clay, C horizon | 2.31 | 79.8 | 72.7 |
| Lake Charles clay, surface | 2.95 | 42.4 | 38.9 |
| Clyde clay, surface | 8.40 | 51.7 | 48.6 |
| Lindly sandy loam, surface | 2.38 | 29.2 | 23.4 |
| Davidson loam, surface | 5.58 | 43.3 | 36.7 |
| Clinton silt loam, surface | 1.97 | 28.2 | 23.4 |
| Putnam silt loam, surface | 2.40 | 24.2 | 20.5 |
| Barnes loam, subsoil | 2.98 | 32.2 | 29.2 |

## SUMMARY

A successful method of distillation is presented for determining the combined water in soils.

The soil is placed in a bomb and heated at a high temperature. The combined water is distilled over very rapidly, condensed, and caught in carbon tetrachloride.

Because the combined water can be determined, the ignition method now becomes more accurate and reliable for determining the organic matter in soils.

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PLATE 1

BOMB USED FOR DETERMINING COMBINED WATER BY DISTILLATION

# ON THE DETERMINATION OF THE ION EXCHANGE CAPACITY OF SOILS

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Many investigations show that the replacement of ions in soils for the purpose of determining their exchangeable quantities presents much difficulty. As it recently was pointed out by Gedroiz (4), one fraction of the cations in soils may be easily replaced by some other, but there exists another part which can only be replaced with considerable difficulty, and the reaction never reaches completion within a reasonable time. Gedroiz, therefore, makes a distinction between *intensively* and *extensively* exchangeable bases in soils. Several works of Goy (5) show interesting data along these lines on the exchangeable H ions of soils. On the above basis the author drew a distinction between "easily soluble acid" and "difficulty soluble acid" in soil ("leichtlösliche Säure" and "schwerlösliche Säure"). Kappen drew a similar distinction between "exchange acidity" and "hydrolytic acidity" several years ago.

There is, however, no justification for such arbitrary distinctions. The ion exchange reactions in soils and in other colloidal materials capable of ion exchange seem to follow the laws valid in the case of any reactions influenced by different degrees of dissociation of the reacting ions, as has been shown in several papers by Mattson (9). Results published by the author some time ago (1) also showed that, in respect to the reagent used to effect the H ion exchange, the higher its ratio to the amount of soil taken, the higher the amount of exchanged H ions, and in the case of each soil the graphical representation of the relation between the amounts of exchanged ions and the quantity of replacing reagent used, is a very regular adsorption curve. Vageler and Woltersdorf (13) in a theoretical discussion of these experimental results and of the results of other workers have shown that the curve is a hyperbola corresponding to the hyperboloid form of the dissociation residue curve, and can be characterized by the asymptote formula of the hyperbola as follows:

$$y = \frac{x \cdot S}{x + C}$$

where $x$ = the quantity of reagent used for ion exchange, expressed in milligram equivalents;

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$y$ = the exchanged ions found, expressed in milligram equivalents;
$S$ = the limiting value of the adsorption capacity with respect to the replacing ion;
$C$ = the half value of the limiting value.

If, instead of using the actual values, the reciprocal values are used, the graph becomes a straight line, which can be represented by the following formula:

$$b = K + q\,a$$

Where $b = \frac{1{,}000}{y}$; $K = \frac{1{,}000}{S}$; $a = \frac{1{,}000}{x}$; $q = \frac{C}{S}$.

The $q$ value—the tangent of the angle of inclination—can be calculated from two determinations, which give two points on the hyperbola (i.e. on the straight line, if the reciprocal values are taken), as follows:

$$q = \frac{b_1 - b_2}{a_1 - a_2}$$

It therefore follows that *no absolute value* can be obtained for the end of the ion exchange reaction at any finite dilution, but Vageler and Woltersdorf consider that *comparable values for ion exchange capacity of different complexes are represented by the limiting values* calculated on the foregoing basis (13, 14). In a subsequent publication (12) Vageler points out that the $q$ value "probably represents the reciprocal of a value which seems to be proportional with the dissociation constant of the colloid."

A. Bernolak and the author have obtained further data along this line on eight unsaturated soils obtained from areas which differed widely in all soil characteristics.

A description and some characteristic data for these soils are given in table 1.

These data show that these soils differ widely in their properties.

In order to determine the $q$ value with respect to the exchangeable H ions of these soils, the same amount of soil was treated with two different quantities of a normal calcium acetate solution and the mixtures were allowed to come to equilibrium, then filtered, and the increase of H ions in the filtrate was determined by titration. The $q$ values were calculated by substitution in the formula. The data are given in table 2. In figure 1 the $q$ values are plotted against the quantity of exchanged H ion found with a 1:2.5 ratio of soil to reagent. (The quantity of soil is expressed in grams on 105°C. oven-dry basis, the quantity of reagent in milligram equivalents of a normal solution, respectively.)

From this curve the $q$ value appears to be intimately correlated with the H ions exchanged at a certain ratio, irrespective of the nature of the soil and seems to be, therefore, a function of the degree of dissociation of the acidoid alone, i.e., of the activity of exchangeable H ions present in the complex. In other words: *those quantities of soils or other materials capable of ion exchange, which*

*are equivalent with respect to their ion exchange capacities must show the same ion exchange, if treated with the same amount of replacing reagent.*

TABLE 1

*General data* on the soils used in the experiments*

| NUMBER | DESCRIPTION OF THE SOILS | pH (IN WATER SUSPENSION) | EXCHANGEABLE CATIONS ($S$ ACCORDING TO HISSINK) | ($T$-$S$) (EXCHANGEABLE $H^+$) | $T$ (CATION-EXCHANGE CAPACITY) | $V$ $100\ S/T$ |
|---|---|---|---|---|---|---|
| | | | m.e. per 100 gm. soil 1:105°C. oven-dry | | | |
| | | | | | | *per cent* |
| 59 | Sand, very low in organic matter | 7.02 | 2.04 | 2.50 | 4.54 | 44.9 |
| 51 | Sand, very low in organic matter | 6.56 | 1.80 | 2.58 | 4.38 | 41.1 |
| 88 | Sand, low in organic matter | 6.11 | 2.88 | 4.03 | 6.91 | 41.7 |
| 190 | Clay, low in organic matter | 4.87 | 20.80 | 11.21 | 32.01 | 65.0 |
| 431 | Clay, low in organic matter | 5.89 | 37.38 | 12.45 | 49.83 | 75.0 |
| 16 | Loam, low in organic matter | 6.01 | 19.40 | 6.57 | 25.97 | 74.7 |
| 1198 | Clay loam, medium in organic matter | 6.05 | 30.50 | 17.23 | 47.73 | 63.9 |
| 1404 | Loam, rich in organic matter | 6.85 | 47.36 | 14.06 | 52.02 | 91.0 |

* The exchangeable bases have been obtained by electrodialysis; the ($T$-$S$) values are calculated on the basis of the hydrolytic acidity according to Kappen (7). $T$ and $V$ values, according to Hissink (6), have been calculated on the basis of the values obtained by the above determinations.

TABLE 2

*Exchanged $H^+$ at different soil reagent ratios*

| NUMBER | EXCHANGED $H^+$ M.E. PER 100 gm. 105°C. OVEN-DRY SOIL | | $q$ |
|---|---|---|---|
| | 1:2.5 ratio, gm. m.e. soil: reagent | 1:25 ratio, gm. soil: m.e. reagent | |
| 59 | 0.77 | 2.71 | 258.3 |
| 51 | 0.79 | 2.86 | 254.5 |
| 88 | 1.24 | 2.91 | 128.6 |
| 190 | 3.45 | 8.50 | 47.9 |
| 431 | 3.83 | 8.67 | 40.5 |
| 16 | 2.02 | 5.87 | 90.2 |
| 1198 | 5.30 | 10.00 | 24.6 |
| 1404 | 1.25 | 3.00 | 129.6 |

Results obtained for the ion exchange capacity by any method can be checked up on this basis by weighing out quantities of the materials, which, according to the results obtained by the method in question, should be equivalent with respect to their ion exchange capacities. If the method gave the correct, i.e., comparable, results, equal amounts of exchanged ions must be found, if equivalent weights of soils have been treated with equal amounts of reagent.

We carried out experiments with our soils along this line. A method for the determination of the exchangeable H ions in soils suggested by the author (1) was used. Quantities of soils which were equivalent with respect to their exchangeable H ions were calculated and weighed out according to the results obtained by this method, and treated in one series with 250 cc. and in another

TABLE 3

*Comparison of results of exchangeable $H^+$ on equivalent quantities of soils*

| NUMBER | EXCHANGEABLE $H^+$ M.E. PER 100 GM. 105°C. OVEN-DRY SOIL ACCORDING TO THE AUTHOR'S METHOD | EQUIVALENT WEIGHTS: (QUANTITY OF SOIL CORRESPONDING TO 1:88 M.E. OF EXCHANGEABLE $H^+$) | EXCHANGED $H^+$ IN M.E. PER EQUIVALENT WEIGHTS | |
|---|---|---|---|---|
| | | | 250 cc. of replacing reagents per equivalent weight | 250 cc. of replacing reagents per equivalent weight |
| | | *grams* | | |
| 59 | 2.63 | 71.48 | 0.69 | 1.70 |
| 51 | 1.88 | 100.00 | 0.70 | 1.70 |
| 88 | 2.38 | 78.99 | 0.69 | 1.72 |
| 190 | 20.50 | 9.17 | 0.89 | 2.50 |
| 431 | 13.50 | 13.93 | 0.89 | 2.50 |
| 16 | 10.50 | 17.90 | 0.88 | 2.50 |
| 1198 | 27.50 | 6.84 | 0.89 | 2.50 |
| 1404 | 7.50 | 25.07 | 0.88 | 2.50 |

with 2,500 cc. of a normal calcium acetate solution. The data of this experiment are shown in table 3. The results show extremely good agreement, the soils, however, fall into two groups: (*a*) Sandy soils very low in exchangeable H ions, which give a good agreement amongst themselves, give uniformly lower results, if compared with the other group; (*b*) loam and clay soils high in exchangeable H ions also show good agreement among themselves but give higher results than the soils of the former group.

Subsequent experimental work carried out by the author at the New Jersey Agricultural Experiment Station has shown that this difference arises from the fact that a comparatively large amount of sandy soil has to be taken to give equivalents of exchangeable H ions with the loam and clay soils. With the loam and clay equivalent weights the results are obtained therefore from considerably lower soil/reagent ratios than with the sand equivalent weights, and the results on such a basis are not strictly comparable, as was shown by the following experiment:—Twelve very different electrodialyzed soils and other

colloidal materials were used and the displacement of H ions by Ba ions from a normal barium acetate solution was determined at three different ratios. Then the $q$ values were calculated, first from the two higher, and afterwards from the two lower ratios. These values were plotted against the amounts of H ions exchanged at the higher ratios, in figure 2, in the same way as in the figure 1. The graph shows very well that the same results cannot be obtained, if the values are calculated from results obtained at extremely different ratios,

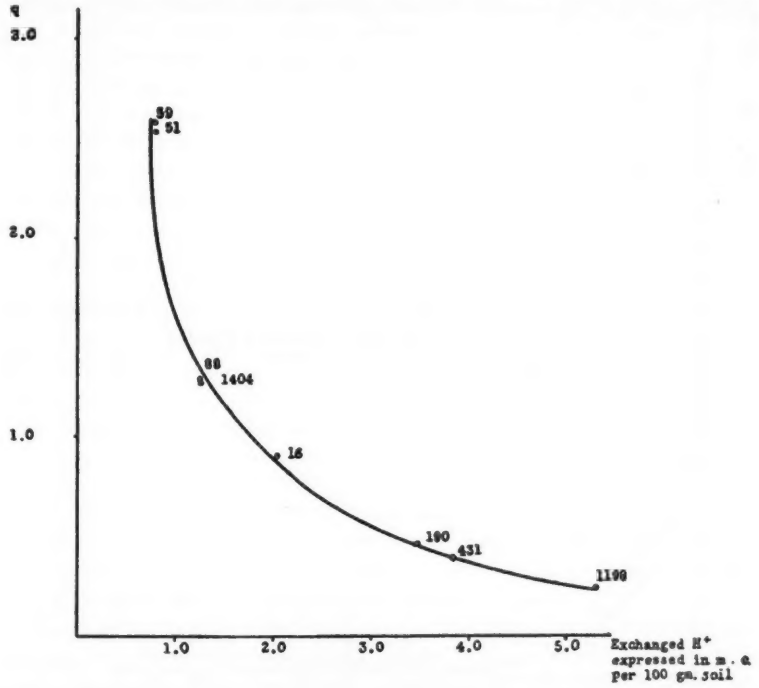


FIG. 1. RELATIONSHIP BETWEEN $H^+$ EXCHANGED 1:2.5 SOIL/REAGENT RATIO AND THE $q$ VALUE (EXPERIMENTAL SOILS)

and that the shifting of the results *is different* in the case of materials with low and high ion exchange capacities. The lower the ion exchange capacity, the higher the increase of the $q$ values, if calculated from lower and lower ratios. Hence, the difference obtained with the ($a$) and ($b$) groups of soils in the case of the experiment described in the foregoing. If we look at the curves of figure 2, and consider their relationship with the experiment described, we find that the results obtained with the loam and clay soils must lie on curves corresponding with the B curve of figure 2 (low soil/reagent ratio), whereas the results of the sandy soils must lie on curves corresponding with the A curve

(high soil/reagent ratio). Therefore the ion exchange of equivalent quantities must have been lower in the case of the soils of the (*a*) group than in the case of the soils of the (*b*) group.

It still must be pointed out that the relation between the *q* value and the ion exchange at a certain ratio does not agree as well, if the comparison is made on the basis of results obtained by very diluted suspensions (low soil/reagent ratios). The *q* values calculated by the results of the 1:20 and 1:100 dilutions give considerable irregularities with respect to this relationship, as is shown by

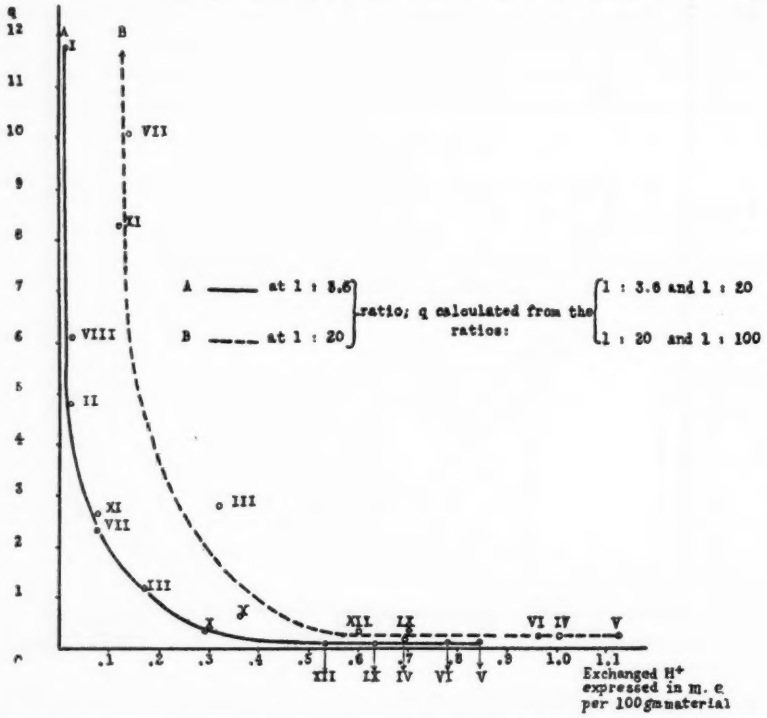
q
A —— at 1 : 5.6
B ---- at 1 : 20
ratio; q calculated from the ratios:
1 : 5.6 and 1 : 20
1 : 20 and 1 : 100
Exchanged H+ expressed in m. e per 100 gm material

FIG. 2. RELATIONSHIP BETWEEN $H^+$ EXCHANGED AT DIFFERENT MATERIAL/REAGENT RATIOS AND THE *q* VALUE (SOILS AND OTHER COLLOIDS)

curve B in figure 2. It seems that the concentration of the suspension itself influences the results *to a comparatively small extent*, and this influence may, in all probability, vary according to the nature of the physical properties of the material. Besides this, the adsorption curve may still be affected by other factors, namely, by reactions and dissociation phenomena of the other ions present; for example, by anion exchange.

Nevertheless we can see that the influence of the exchangeable amount of the investigated ion present, i.e., its power to dissociate, suppresses almost all

the influences of this kind, at least at high material/reagent ratios. If so, we have the possibility of estimating equivalent amounts of different materials with respect to their exchangeable ion by interpolation, i.e., by calculation with the formula of the adsorption curve. Equal amounts of exchanged ions must belong to equivalent quantities, if the same amounts of replacing reagent are used, as this was shown. Hence, in order to obtain equal amounts of exchanged ions, different quantities of reagent must be taken. *The quantities of reagent used to obtain equal base exchange must be proportional to the equivalent weights.* The equivalent weights cannot be determined on this basis experimentally because of the already described shifting of the curves, unless the factors affecting this shifting and their quantitative influences are not determined. The calculation of any points on the adsorption curve, however, must give correct results for the purpose of comparison of ion exchange at any ratios if the fundamental requirement is fulfilled, namely, that the $q$ values calculated from the points determined show a regular decrease in proportion with an increase of the amounts of exchanged ions of the different materials at a certain material/reagent ratio.

The agreement of the results with our experimental soils can be considered to be only approximate from this point of view; probably because the effects described in the foregoing influenced the results to some extent in the case of these very different soils and with the applied ratios. Yet, a comparison of the equivalent weights calculated on the basis of the adsorption curves with the experimental results obtained by independent methods show fairly good agreement even in this case. The data for this comparison have been obtained by a method described in the following.

The exchangeable H ions of the soils were determined by several other methods, which have been recently used for this purpose. The results obtained are given in table 4 and show that a good parallelism of the results was obtained with all of those methods which are based on the determination of replacement of H ions by the metallic cation until a certain pH value is reached (methods of Jensen, Goy, and the author). All the other methods which are based on a direct comparison of the amounts of exchangeable H ions on the basis of the results of a determination of the exchanged H ions at a certain prescribed soil/reagent ratio gave results which often show very considerable discrepancies in comparison with the aforementioned methods. It is also obvious from this that these methods are based on an erroneous assumption, since no comparable results can be obtained if only one arbitrary point of the adsorption curve is taken. Also, by the calculation of the limiting values erroneous results were obtained. This is natural, since this value can only be regarded as representing the *comparative* maximum replaceability of H ions *by the cations of the particular solution* being used. The end of the reaction could be found only if an infinitely large quantity of reagent were used, and, therefore, equal pH values with the different materials can never be reached at any finite dilution. Therefore, *finite values* calculated on this basis must be erroneous *from the point of view of*

*comparison of the exchangeable ion* present in the different complexes. This has already been pointed out and shown experimentally in an earlier publication by the author (3).

Now there have been calculated the amounts of reagent which are necessary to obtain equal amounts of exchanged H ions with the different complexes on the basis of the adsorption curve by the formula suggested by Vageler and Woltersdorf. On the basis of two points of the curve given in table 2, $a$, $b$, $q$, and $k$ values were calculated; then $a_3$ and $x_3$ values were calculated, taring $b_1 = 500$, $y_1 = 2.0$, respectively, in all of the cases. On the basis of $x_3$ values (i.e., the amounts of reagent necessary to obtain 2.0 m.e. of exchanged H ions

TABLE 4

*Comparison of the results obtained by different methods for the exchangeable $H^+$*

| NUMBER | EXCHANGEABLE $H^+$ IN M.E. PER 100 GM. 105°C. OVEN-DRY SOIL | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Hissink 0.55 $T$-$S$ (about pH 8) | Hutchinson-McLennan (about pH 7) | Kappen | | Vageler and Woltersdorf limiting value (about pH 8) | Jensen | | Goy (pH 7 in N K Cl suspension) | The author (pH 8) |
| | | | About pH 7 | About pH 8.5 | | pH 7 | pH 8 | | |
| | | | | | | In water suspension | | | |
| 59 | 1.39 | 0.60 | 1.15 | 2.50 | 3.77 | 0.50 | 2.75 | 2.00 | 2.63 |
| 51 | 1.12 | 0.80 | 1.19 | 2.58 | 4.03 | 0.25 | 2.00 | 1.75 | 1.88 |
| 88 | 2.88 | 1.00 | 1.86 | 4.03 | 3.42 | 1.50 | 2.90 | 2.75 | 2.38 |
| 190 | 19.79 | 3.50 | 5.18 | 11.21 | 10.20 | 10.00 | 20.0 | 20.00 | 20.50 |
| 431 | 11.50 | 3.80 | 5.75 | 12.45 | 10.10 | 7.50 | 15.50 | 14.50 | 13.50 |
| 16 | 6.51 | 2.20 | 3.03 | 6.57 | 7.46 | 5.00 | 10.00 | 9.50 | 10.50 |
| 1198 | 14.53 | 4.60 | 7.95 | 17.23 | 11.11 | 10.00 | 25.00 | 25.0 | 27.50 |
| 1404 | 0.00 | 1.12 | 1.88 | 4.06 | 3.55 | 2.25 | 7.00 | 7.00 | 7.50 |

in all cases) the equivalent weights were calculated, soil 51 being taken as the basis, as follows:

$$\text{Equivalent weight} = \frac{100 \cdot x_3}{x_3 \text{ with soil 51}}$$

The results obtained by this calculation and the equivalent weights calculated from the results obtained by Kappen's method, by the limiting values, and by the author's method are given in table 5.

A rather good agreement between the results obtained by calculation from the curves and those based on the author's method can be found, and although this is only rough, there being even wide discrepancies in two cases (soil 1404 and 59), this comparison seems to strengthen the foregoing statements, as the discrepancies are most likely due to the aforementioned disagreements of the points on the adsorption curves. No correlation can be found in the case of the equivalent weights calculated on the basis of the limiting values, but some interesting confirmations between the interpolated values and the results obtained by Kappen's method can be observed. This fact has a natural

explanation, as these results represent values on the steep part of the adsorption curve where the varying amounts of the exchanged ion often are almost proportional with the ion exchange capacities. The incomparability of the results only becomes more marked when the materials vary greatly in their exchangeable H ions, as is well illustrated by the data in table 5. This is the reason why the unsaturation and lime requirement of soils often can be well characterized for practical purposes by the simple determination of the "hydrolytic acidity" according to Kappen (2, 11). The limiting value does not have this advantage, of course. It shows entirely erroneous values from the point of view of the determination of the amounts of metallic cation necessary to replace H ions until equal pH values are reached, i.e., from the point of view of lime requirement determination. The explanation of this fact has been offered in the foregoing, and is further substantiated by the present data.

TABLE 5

*Comparison of the equivalent weights of the soils with respect to their exchangeable $H^+$ calculated by the different determinations*

| NUMBER | OBTAINED BY INTERPOLATION FROM THE ADSORPTION CURVE | AUTHOR'S METHOD | LIMITING-VALUE OF THE ADSORPTION CURVE (VAGELER'S METHOD) | KAPPEN'S METHOD |
|---|---|---|---|---|
| 59 | 108.8 | 71.48 | 106.89 | 103.20 |
| 51 | 100.0 | 100.0 | 100.00 | 100.00 |
| 88 | 58.2 | 78.99 | 117.8 | 64.01 |
| 190 | 11.8 | 9.17 | 39.51 | 23.01 |
| 431 | 10.0 | 13.93 | 39.90 | 20.72 |
| 16 | 24.4 | 17.90 | 54.02 | 39.27 |
| 1198 | 5.9 | 6.84 | 36.27 | 14.97 |
| 1404 | 58.9 | 25.06 | 113.14 | 63.55 |

It must be clarified by further experiments, whether or not we shall be able to obtain adsorption curves due only to the dissociation phenomena of the investigated ions, i.e., independent of physical effects or other ion reactions—since these would enable us to determine the comparative ion exchange capacities of any complex exactly and in the simplest way and to establish accurate comparative values for the dissociation constant of colloidal ionogens.

According to the foregoing, even those methods for the determination of the base exchange capacity of soils which are based on the ideas of Kelley (8) may not give perfect results, unless the replacement of the adsorbed cations is effected by a replacing reagent with well-established pH, the treatment being continued until the original pH value of the reagent is reached. By the use of a large excess of replacing reagent and by other supplementary treatments designed to bring the base exchange reaction to completion, useful results can be obtained, as the error is eliminated to a considerable extent, but the reaction never can be brought to a real completion. The determination of the displaced cations from the material will, therefore, always be susceptible to more or less

error. This error may some time be considerable. Kelley himself observed and pointed out that it may happen that the replacement cannot be brought to completion (8). Besides, a long treatment and leaching are not desirable at all and cannot be applied in some cases, because they may easily affect considerable changes in the structure of the complex, as has been pointed out by Mattson (10).

SUMMARY

It was shown that the quantities of exchanged ions of soils treated with increasing amounts of replacing reagent are almost independent of specific soil properties and are influenced by the present amount of exchangeable ion, i.e., by its degree of dissociation only.

The cation adsorption of soils, if increasing amounts of a replacing reagent (calcium acetate solution) are used, gives, therefore, curves which are hyperboloid and can be characterized according to Vageler and Woltersdorf by their asymptote formulas, and different important values can be calculated from two or more points determined on the curve experimentally.

The comparison of values calculated on this basis with independent determinations of the amounts of metallic cation necessary for the displacement of H ions until equal pH values are reached, shows that the equivalent weights of the different complexes with respect to their exchangeable H ions are proportional to the calculated ratios of soil to reagent necessary to effect the same amount of cation exchange.

It seems to be probable that the comparability of the adsorption curves suffered to some small extent because of an influence of the physical properties of the different materials and because of other ionic reactions. A further experimental study along this line is necessary to show whether or not quantitative determinations of exchangeable ions and comparative determinations on ionization of colloidal ionogens can be made on this basis.

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# SOME TRANSFORMATIONS OF UREA AND THEIR RESULTANT EFFECTS ON THE SOIL[1]

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Urea was first discovered in urine by Ronelle in 1773, and was first made from isocyanate of ammonia by Wöhler (21) in 1828. In recent years urea has been synthesized on a commercial scale from calcium cyanamid by various processes which have been patented. Kras, Gaddy, and Clark (11) have also developed a process for its synthesis directly from liquid ammonia and carbon dioxide.

The various processes for the synthesis of urea on a commercial scale have probably been the outgrowth of the rapidly increasing interest in concentrated fertilizers, and the realization that urea would probably be one of the more important nitrogen carriers of the future.

Urea is a compound which analyzes 46.5 per cent nitrogen and is the most concentrated form of nitrogen used as a fertilizer at the present time.

The value of a fertilizer material depends upon the changes which it undergoes in the soil, the availability of the transformation products to the plant, and the resultant effects of the products on the soil. Therefore, a study of the changes which the material undergoes in the soil is of fundamental importance from a scientific viewpoint.

## REVIEW OF LITERATURE

Pasteur (19) in 1860 was the first to recognize that the transformation of urea to ammonia is brought about by a living organism—*Torula ammoniacale*. It was later discovered that organisms capable of decomposing urea are found in most families of bacteria, actinomyces, and fungi. But certain specific bacteria whose metabolism is closely connected with this substance are called urea bacteria. The optimum temperature for the action of these organisms is about 30°C., and they usually thrive best in a medium made alkaline with ammonium carbonate. However, it has been found that the accumulation of ammonium carbonate from the hydrolysis of the urea is so great in many instances as to kill the organisms themselves.

Microörganisms capable of decomposing urea are found in manure, dust, and water. Miquel (19) found urea organisms in the canal waters of Paris. He also found that the urea organisms of the surface soil were 1 to 2 per cent of the total bacteria, and that manure and urine contain 10 per cent of their flora as urea bacteria. The air of Paris was found to contain one urea splitting organism for every 67 other forms.

Littauer (13) found that the rate of urea decomposition to ammonia was dependent on the soil type, soil moisture, and temperature. He also observed that urea was decomposed more

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[2] Assistant chemist. The writer takes this opportunity to thank Dr. R. W. Ruprecht, and Dr. R. M. Barnette, under whose direction this investigation was conducted, for their helpful suggestions and kindly criticisms, for the facilities made available, and for reading the manuscript. Thanks are also extended to the Synthetic Nitrogen Products Company for providing the funds which made this study possible.

rapidly in a loam soil; and, although drought retarded the rate, increasing the soil moisture above 50 per cent of its maximum water-holding capacity did not cause any significant change in the rate of decomposition.

Brioux (3) states that urea is rapidly transformed into ammonia and acts very much as a physiologically alkaline fertilizer, but later reacts very much as a physiologically acid fertilizer when the ammonia is nitrified.

Lipman and McLean (12) produced experimental evidence to prove that urea manufactured from cyanamid does not give as good results as urea made directly from ammonia and carbon dioxide. They explained this as being due to the presence of dicyanodiamide and guanyl sulfate, which have a toxic effect on plants.

Prince and Winsor (16) investigated the rate of decomposition of urea in cultures containing different percentages of soil and sand. About 10 per cent moisture was used in sand cultures, and 15 per cent in half sand and half soil. The cultures were maintained at room temperature. The index for determining the rate of decomposition of urea was the amount of ammonia present in the cultures at different periods of time. After 5 days they found that only 3 per cent of the urea was converted to ammonia in the sand cultures, 67 per cent in half sand and half soil, and 90 per cent in soil alone.

Bordas and Mathieu (2) investigated the transformation of urea to ammonia by the addition of the enzyme urease (extracted from soybeans) to an aqueous solution of urea. They found that approximately 95 per cent of the urea was hydrolyzed by the urease within 48 hours at 17°C. They also added fermented urine and manure extract to a soil which contained urea. They found increased amounts of ammonia in the presence of these ferments.

The nitrogen transformation in the soil which is most essential for plant growth is the oxidation of ammonia to nitrates. It has been observed that plants absorb nitrogen in the form of ammonia to a limited extent, depending on the stage of growth of the plants. Plant physiologists in general recognize that nitrate nitrogen is the form most available for plant growth.

Smith (18) observed that the optimum soil moisture content for nitrate production from various nitrogenous materials was between 50 and 60 per cent of the maximum water-holding capacity of Norfolk sandy loam soil. However, he obtained a larger nitrate accumulation from urea at 70 per cent of the water-holding capacity of the soil than from ammonium sulfate, dried ground fish, or packing house tankage. He is also of the opinion that after the first period of rapid nitrification the fluctuations of nitrate nitrogen in the soil are due to the action of soil microörganisms rather than to differences in soil moisture, temperature, or reaction.

## OBJECTS OF STUDY

The objects of the present study on urea were to determine the influence of soil moisture, time, concentration of urea in the soil, and temperature, on the rate of transformation of urea to ammonia and subsequently to nitrates. The acidity relationships produced in the soil as the result of accumulated products, ammonia and nitrates, were studied under both unleached and leached conditions of the soil. These studies were carried out altogether in soil cultures.

## EXPERIMENTAL METHODS

### *Method of culture*

All soil cultures were prepared with Norfolk fine sand collected from an uncultivated area which was growing to broomsedge grass. The surface 8 inches of soil was removed, thoroughly mixed, sieved, and dried under atmospheric conditions to air-dry basis.

The cultures were prepared by thoroughly mixing given quantities of urea with 5 kgm. of air-dry soil and placing the mixture in 1-gallon glazed pots, which previously had been weighed. For each pot culture to which urea was applied, a culture was prepared which contained only soil. The calculated amount of water was added to each culture to bring it to the desired soil moisture content. The total weight of the pot, soil, and water being known, the cultures were weighed at periodic intervals and the water lost by evaporation was replaced.

### *Method of sampling*

A representative sample of soil was obtained by making a number of borings from the top to the bottom of each culture with a small metal tube about one-half inch in diameter. Thus several cylindrical portions of soil were removed from different parts of the pot. The sub-samples were thoroughly mixed, and duplicate samples to be analyzed were weighed from the composite. Samples on which the pH was determined were also obtained from this composite.

### *Chemical methods*

Since chemical determinations were made in duplicate on each soil culture, and a large number of cultures were maintained, it was necessary to use relatively simple methods of analysis. Upon investigation there did not seem to be a method for the determination of ammonia in the presence of urea which would meet these requirements. However, three possible methods were selected and compared. The methods were as follows: Distillation with magnesium oxide as described by Emerson (5); Aeration as described by Mathew (14); Displacement of ammonia from the soil by leaching with a salt solution.

Comparable results were obtained with all three of these methods. The aeration method was eliminated, for it became evident that it was not suitable for making a sufficient number of determinations simultaneously.

The results which were obtained by distillation with magnesium oxide did not indicate that urea was broken down by the heat of distillation. However, Emerson (5) suggests that the determination of ammonia in soils by the aid of heat at the boiling temperature is questionable, for some amino acids are usually present and may be decomposed.

It was found to be more convenient to analyze a large number of samples at one time by displacing the ammonia from the soil with a N solution of sodium sulfate. This method consisted of transferring 25-gm. samples of soil to filters and leaching with sufficient N sodium sulfate solution to give 250 cc. of percolate. The percolate was collected in 250-cc. volumetric flasks and thoroughly shaken to insure a uniform distribution of ammonia in solution. Aliquots were removed from the flasks, placed in graduated cylinders, diluted, and nesslerized.

Since this method gave comparable results with sandy soil, and did not involve any process of heat, it seemed to be the more logical method to use.

Nitrates were determined by the phenol disulfonic acid method on aliquots of a 1 to 5 soil extract as described by Schreiner and Failyer (17).

The hydrogen-ion concentration was determined by the quinhydrone electrometric method in a 1 to 2 soil-water suspension.

## EXPERIMENTAL RESULTS

### *Influence of soil moisture and time on the rate of conversion of urea*

The series of cultures used in this experiment were maintained at a constant temperature of 21°C. for 34 days, from February 25 to April 4, 1930. The

TABLE 1

*Treatment of soil cultures maintained for 34 days at 21°C.*

| POT NUMBER | TREATMENT | MOISTURE* |
|---|---|---|
| | | *per cent* |
| 1 | None | 3.80 |
| 2 | 1 gm. urea | |
| 3 | None | 6.80 |
| 4 | 1 gm. urea | |
| 5 | None | 9.00 |
| 6 | 1 gm. urea | |
| 7 | None | 11.70 |
| 8 | 1 gm. urea | |
| 9 | None | 13.95 |
| 10 | 1 gm. urea | |
| 11 | None | 15.85 |
| 12 | 1 gm. urea | |
| 13 | None | 17.95 |
| 14 | 1 gm. urea | |
| 15 | None | 20.55 |
| 16 | 1 gm. urea | |

* Percentage of moisture on the dry basis of the soil.

treatments of the different cultures, with regard to urea and moisture, are shown in table 1.

Ammonia determinations were made on samples collected from each of these cultures at periodic intervals. The first determinations were made approximately 24 hours after sufficient water was added to adjust the cultures to their respective soil moisture contents. Ammonia was determined as parts per million in a sodium sulfate soil percolate and calculated to milligrams of ammonia per 100 gm. of dry soil. The quantity of ammonia which accumu-

lated from urea was calculated by subtracting the quantity in the check cultures from the quantity in the cultures of the same moisture content and treated with urea.

The results thus obtained on different dates in cultures of the same soil moisture content were averaged by means of a moving average. This was done in order to remove the unevenness between the determinations on different dates, due to causes inherent in the cultures themselves and not dependent on the factors which were under consideration. In the use of the moving average the quantities of nitrogen in each soil moisture content, for three consecutive dates of determination, were added and divided by 3. The average value obtained was considered to represent the quantity of nitrogen as ammonia for the middle date. The average values thus calculated are presented in the ammonia nitrogen plane of figure 1.

One set of surface lines in figure 1 represent the effect of variable soil moisture contents on the accumulation of ammonia at given times. The other set of lines represent the effect of time on the transformation of urea to ammonia in each culture of a given soil moisture content. The rate of accumulation of ammonia from urea was greatest in the soil cultures of low soil moisture contents, and apparently decreased as the soil moisture increased to 13.95 per cent. It again increased up to a soil moisture content of 15.85 per cent and decreased from this point to 20.55 per cent.

The surface lines for given soil moisture contents, time being variable, show that urea was rapidly decomposed to ammonia immediately after application to the soil. And the soil at all moisture contents shows a gradual accumulation of ammonia from urea during the first 20 days of incubation. After 20 days the ammonia content either remained about constant or decreased in all cultures except that of 20.55 per cent moisture.

The soil was approximately saturated at 17.95 per cent moisture and at 20.55 per cent it was submerged under water. Consequently, at 20.55 per cent moisture the biological activity was that of anerobic conditions.

The rate of accumulation of ammonia from urea at the different soil moisture contents is misleading unless the possible oxidation of some of the ammonia to nitrates is considered.

Nitrate determinations were made on soil samples from the cultures previously described at periodic intervals of one week over the period of incubation. The quantity of nitrate which was formed from urea in the different soil moisture contents was calculated as has been described for ammonia and expressed as milligrams of nitrogen per 100 gm. of dry soil.

The results obtained by the moving average are presented in the nitrate nitrogen plane of figure 3.

In figure 3 the heights of the surface lines for given times show that there was no significant increase in the nitrate content of the soil until 17 days after incubation commenced. After 17 days the rate of accumulation of nitrates was comparatively rapid. This is shown by the height of curves for 24 and 31 days

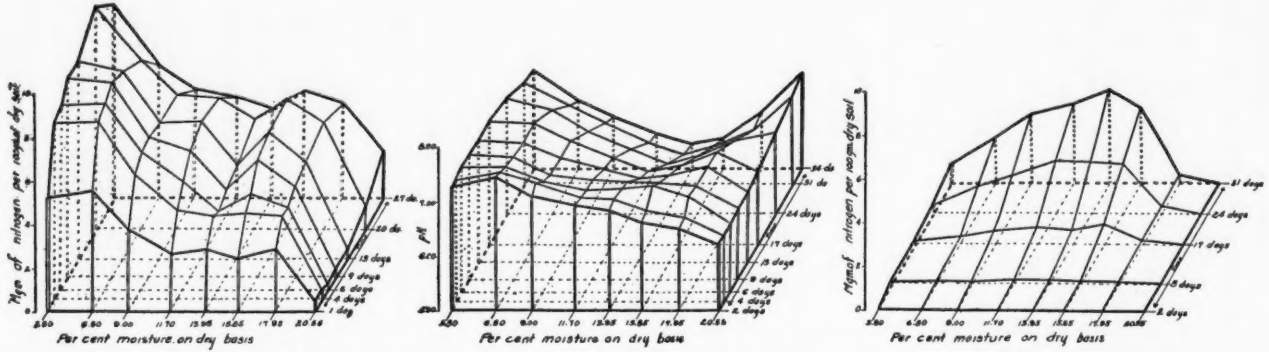



FIG. 1 FIG. 2 FIG. 3

THE EFFECT OF TIME AND MOISTURE ON THE CONVERSION OF UREA TO AMMONIA NITROGEN AND NITRATE NITROGEN, AND THE SUBSEQUENT EFFECT OF THE ACCUMULATION OF THESE PRODUCTS ON THE HYDROGEN-ION CONCENTRATION OF SOIL CULTURES

(5 kgm. of Norfolk sand and 1 gm. of urea maintained at a constant temperature of 21°C.)

respectively. The rate of nitrification increased directly as the soil moisture increased to 13.95 per cent. From 13.95 to 20.55 per cent moisture the rate of nitrification decreased as the soil moisture increased.

Therefore, 13.95 per cent seems to be the optimum moisture content for the nitrification of urea in Norfolk sand, when the temperature is controlled at 21°C.

In the transformation of urea to ammonia and the subsequent oxidation of the ammonia to nitrate, two counteracting chemical compounds are formed which influence the acidity relationships in the soil. It has been shown that the accumulation of ammonia and nitrate is dependent on the soil moisture content and the time. Consequently, there should be some correlation between the quantities of the respective compounds at the different soil moisture contents and the different times, with the acidity relationships in the soil.

The pH value of the soil was determined on soil samples from each of the cultures previously described on each date that either ammonia or nitrates were determined. The pH values were also averaged by the moving average, and the averaged results are presented in the pH plane of figure 2.

The surface lines for given times show the effect of soil moisture on the pH value of the soil at different times during the incubation period. The surface lines for given soil moisture contents show the effect of time on the pH of the soil for each soil moisture content throughout the period of incubation.

In order to arrive at any conclusions concerning the surface effect of figure 2, both figures 1 and 3 must be correlated with it.

Ammonia, an alkaline compound, and nitrate representing nitric acid; produce converse acidity relationships in the soil. Depending upon the quantities of ammonia and nitrate accumulated in the soil there should be a correlation of the activity of these compounds with the pH value of the soil. The high areas of figure 2 represent the more alkaline condition of the soil, and the lower areas represent the more acid condition. Consequently, there should be a direct correlation between figures 1 and 2, and a corresponding inverse correlation between figures 2 and 3. This correlation holds true in a general way.

Figure 1, which represents the quantity of nitrogen as ammonia in the soil, is high through the area of low soil moisture contents. Figure 3, which represents the quantity of nitrogen as nitrates, is low through the corresponding area; and the pH plane is relatively high through this area. On the other hand, the area of figure 3 which represents relatively high concentrations of nitrogen as nitrate shows a correspondingly lower pH value of the soil through the same area of figure 2. However, at extremely high soil moisture contents, represented by the surface line for 20.55 per cent moisture, the pH value appears relatively high in relation to the quantity of ammonia; but the corresponding line in figure 3 shows that no nitrate was formed under this condition. The indications are that a small amount of ammonia in the absence of nitrates will produce a relatively higher pH value in Norfolk sand of high moisture content than might be expected.

*Effect of increasing the concentration of urea in soil cultures*

The effect of increasing the concentration of urea in the soil was determined by preparing two series of soil cultures. The cultures consisted of equal weights of sieved air-dried Norfolk sand and different quantities of urea. One of the series had the soil moisture contents varied from 10 to 70 per cent of the maximum water-holding capacity of the soil as described by Emerson (5). This series of cultures was placed in the greenhouse where the temperature varied daily. The maximum temperature during the period of incubation, as recorded by a thermograph, was 35°C. while the minimum temperature was about 7°C. The other series prepared in a similar manner, except that the soil moisture was varied from 10 to 60 per cent of its maximum water-holding capacity, was placed in a room with a constant temperature of 21°C. The treatments of the different cultures with regard to urea and moisture are given in table 2.

Nitrates were determined on soil samples from each of these cultures at intervals of 2 weeks over a period of 110 days from October 12, 1929, to January 31, 1930.

The quantity of nitrogen which accumulated as nitrates in the cultures from urea was calculated as previously described.

The results obtained from cultures of 2 gm. and 1 gm. of urea and maintained under variable temperature conditions of the greenhouse are presented in figures 5 and 9, respectively. The results obtained from cultures of similar treatment, but controlled at a constant temperature of 21°C. are presented in figures 7 and 11, respectively.

The pH values were determined on samples from these cultures on the same dates that nitrates were determined, with the exception of the first date after incubation began. The data for these determinations are presented in figures 4, 6, 8, and 10 respectively.

Figures 4, 5, 8 and 9 show the respective pH values and nitrate contents of soil cultures treated with 2 gm. and 1 gm. of urea, respectively, and maintained under greenhouse conditions. Figures 6, 7, 10 and 11 show the respective pH values and nitrate contents of soil cultures treated with 2 gm. and 1 gm. of urea, respectively, and controlled at a constant temperature of 21°C.

There is a correlation between the pH values and the corresponding nitrate contents of the soil. The lines representing the low soil moisture contents range near the bottom of the graphs for nitrogen as nitrate; whereas the corresponding lines of the graphs for pH values range near the top. The inverse correlation between the nitrate content of the soil and its pH value as shown in the three dimensional graphs of figures 2 and 3 is substantiated.

Figures 5 and 9 show the influence of urea concentration on the rate of nitrate accumulation in soil cultures maintained under green-house conditions. Also figures 7 and 11 show the influence of doubling the concentration of urea on the nitrate accumulation in soil cultures controlled at 21°C.

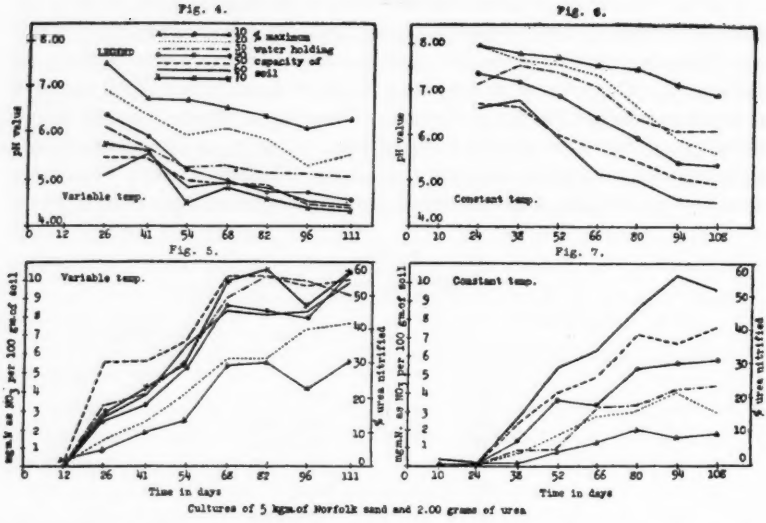
The rate of nitrate accumulation appeared to be slightly more rapid in the cultures treated with twice the amount of urea. However, when the percentage of the urea nitrified is considered, this observation does not seem nearly so significant. The cultures treated with 1 gm. of urea contained 9.2 mgm. of nitrogen as urea per 100 gm. of dry soil. Therefore, in figures 9 and 11, which represent cultures treated with 1 gm. of urea, 9.2 mgm. of nitrogen as nitrate represents 100 per cent nitrification of the urea. Similarly 11 mgm. of nitrogen as nitrate per 100 gm. of dry soil in cultures which received 2 gm. of urea, repre-

TABLE 2

*Treatment of soil cultures*

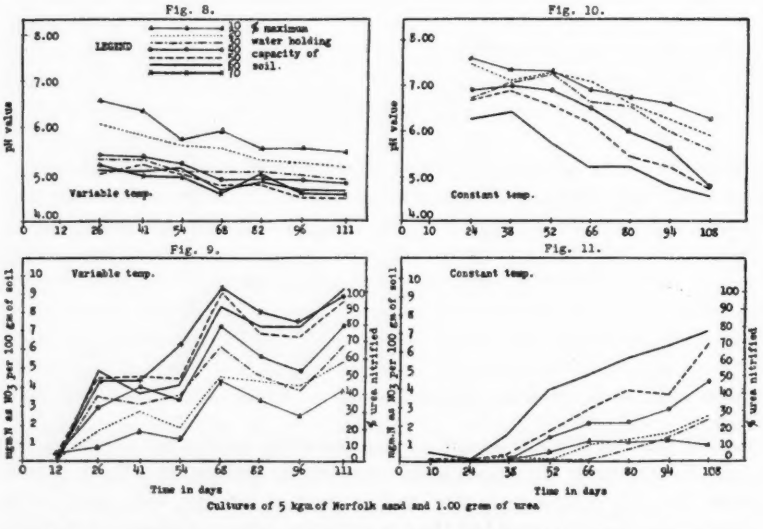
| POT NUMBERS | | TREATMENT | PER CENT MAXIMUM WATER-HOLDING CAPACITY OF SOIL |
|---|---|---|---|
| Greenhouse conditions | Constant temperature | | |
| 1 | 22 | None | 10 |
| 2 | 23 | 1 gm. urea | |
| 3 | 24 | 2 gm. urea | |
| 4 | 25 | None | 20 |
| 5 | 26 | 1 gm. urea | |
| 6 | 27 | 2 gm. urea | |
| 7 | 28 | None | 30 |
| 8 | 29 | 1 gm. urea | |
| 9 | 30 | 2 gm. urea | |
| 10 | 31 | None | 40 |
| 11 | 32 | 1 gm. urea | |
| 12 | 33 | 2 gm. urea | |
| 13 | 34 | None | 50 |
| 14 | 35 | 1 gm. urea | |
| 15 | 36 | 2 gm. urea | |
| 16 | 37 | None | 60 |
| 17 | 38 | 1 gm. urea | |
| 18 | 39 | 2 gm. urea | |
| 19 | | None | 70 |
| 20 | | 1 gm. urea | |
| 21 | | 2 gm. urea | |

sents 60 per cent of the 18.4 mgm. of nitrogen added as urea per 100 gm. of dry soil. Consequently the graphs which represent an application of 2 gm. of urea show that only a little more than half as much of the urea was converted to nitrate as in the cultures of half the concentration, when considered on the basis of the percentage of the urea nitrified.




Cultures of 5 kgm.of Norfolk sand and 2.00 grams of urea

THE EFFECT OF TEMPERATURE AND MOISTURE ON THE CONVERSION OF UREA TO NITRATES AND THE RESULTANT EFFECT ON THE pH OF SOIL CULTURES




Cultures of 5 kgm.of Norfolk sand and 1.00 gram of urea

THE EFFECT OF TEMPERATURE AND MOISTURE ON THE CONVERSION OF UREA TO NITRATES AND THE RESULTANT EFFECT ON THE pH OF SOIL CULTURES

*Influence of temperature on rate of nitrate nitrogen production in soil*

A number of soil investigators have observed that temperature is a factor which controls, in a great measure, the quantity of nitrates produced in unit time. Greaves (7) points out some observations made by Schlösing, as follows: "Schlösing found nitrification very slow at 7.5°C.; quite marked at 11°; reached its maximum at 37°, and ceased entirely at 55°."

Panganiban (15) found that nitrification processes take place between 15° and 40°C. and that the optimum temperature in soil cultures is about 35°C. or slightly higher.

The effect of two temperature conditions on the accumulation of nitrates from urea, is represented by figures 5 and 7 for 2 gm. of urea; and by figures 9 and 11 for 1 gm. of urea. The temperatures used were a constant temperature of 21°C. and the variable temperature of the greenhouse. The 1 gm. urea cultures were selected to show the relation between temperature and nitrate nitrogen accumulation in the soil. The nitrate nitrogen determinations of different soil moisture contents were averaged for each date of determination. This gave a mean nitrate nitrogen accumulation for all the cultures of different soil moisture contents represented in figures 9 and 11. The results calculated for the constant temperature of 21°C. and the variable temperature of the greenhouse are plotted in figure 12.

The thermograph readings showed that the temperature in the greenhouse varied from a maximum of 35°C. to a minimum of 7°C. This was a temperature range of from 14°C. higher to 14°C. lower than the constant temperature of 21°C. The maximum and minimum temperature range alone has little significance in comparing the nitrate accumulations under the two temperature conditions. The length of time that the temperature of the greenhouse ranged higher or lower than 21°C. would be expected to produce a corresponding effect on the nitrate accumulations under that condition.

The average daily temperature of the greenhouse was obtained by tabulating the temperature as recorded on thermograph charts at each 2-hour period of the day. These were added and divided by 12. The quotient was taken as the average temperature of the greenhouse for each day. The data for the averaged daily temperature as calculated are also plotted in figure 12.

Figure 12 shows that the nitrate accumulation in cultures of the greenhouse were much higher than those of the constant temperature condition, but the daily temperature of the greenhouse was not on the average significantly higher than 21°C. However, the 14-day interval between the first and second nitrate determinations show a relatively higher average daily temperature and a correspondingly more rapid nitrate accumulation for greenhouse conditions. Subsequent to the second determination the average daily temperature of the green house was distinctly lower than 21°C., and the nitrate accumulation during this period was practically at a standstill. Between the third and fourth determinations the average daily temperature of the greenhouse was higher than

21°C., and the nitrate accumulations increased rapidly. The next two periods of observation show a distinctly lower average daily temperature in the greenhouse. The result was that the nitrate nitrogen actually decreased in the soil cultures. The final period of observation shows a gradual increase in the average daily temperature, and there was a corresponding increase of nitrate nitrogen in the soil cultures.

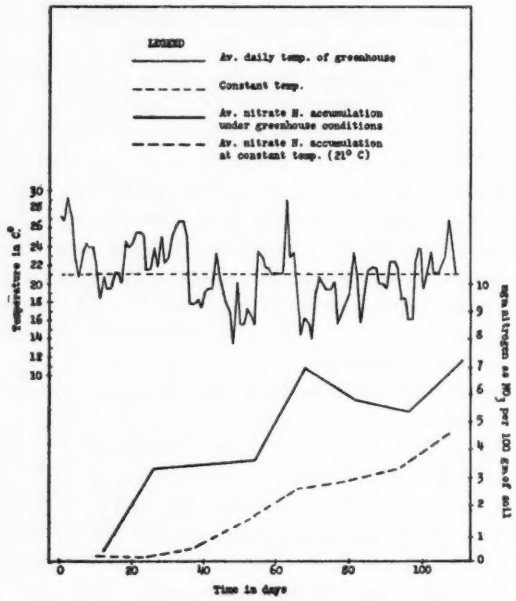



FIG. 12. COMPARISON OF VARIABLE TEMPERATURE OF GREENHOUSE AND CONSTANT TEMPERATURE OF 21°C. ON THE RATE OF CONVERSION OF UREA NITROGEN TO NITRATE NITROGEN

The nitrogen graphs are an average of all nitrate nitrogen accumulations of different moisture contents as shown in figures 9 and 11 respectively. (5 kgm. Norfolk sand and 1.00 gm. urea.)

The indications are that the higher temperature of the greenhouse, immediately after incubation began, stimulated a rapid conversion of the urea to the nitrate form. Consequently, even though lower temperatures than 21°C. tended at times even to decrease the amounts of nitrate nitrogen in these cultures, the gains made in the early periods of incubation were never overcome by the cultures maintained at 21°C. The cultures maintained at 21°C. show a progressive increase of nitrates throughout the period of incubation.

*Effect of leaching the soluble salts from the soil*

Crowther (4) and others have shown that the total soluble salts in a soil affect its pH value depending on the concentration and chemical nature of the salts.

It was observed by Brioux (3) and has been illustrated in figures 1, 2 and 3 that the accumulation of ammonia from urea increased the pH value considerably. On the other hand the accumulation of nitrates decreased the pH value of the soil. However, soil cultures are not comparable to field conditions where

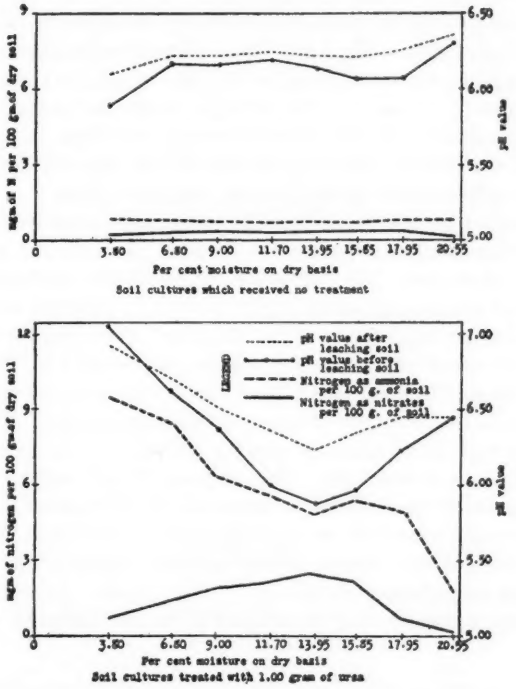

mgs. of N per 100 gms. of dry soil
pH value
3.80
6.80
9.00
11.70
13.95
15.85
17.95
20.95
Per cent moisture on dry basis
Soil cultures which received no treatment
LEGEND
pH value after leaching soil
pH value before leaching soil
Nitrogen as ammonia per 100 g. of soil
Nitrogen as nitrates per 100 g. of soil
mgs. of nitrogen per 100 gms. of dry soil
Per cent moisture on dry basis
Soil cultures treated with 1.00 gram of urea

FIG. 13. EFFECT OF LEACHING THE SOLUBLE SALTS FROM THE SOIL ON ITS pH VALUE AS CORRELATED WITH THE AMMONIA AND NITRATE NITROGEN CONTENT OF THE SOIL

the accumulated products are removed either by the absorption of growing plants or by leaching due to rains. Therefore, it was thought desirable to leach soil samples free of their soluble salts and determine the residual effects of the added urea on the soil. The pH value of the soil was used as an index of the residual effects.

Samples for this observation were obtained from the soil cultures described in table 1. At periodic intervals of about 1 week 25-gm. samples of soil from each

of the cultures were placed on filters and leached with distilled water so as to give 250 cc. of percolate. This quantity of water was found to be sufficient to remove practically all the nitrate salts from the soil. A portion of the soil, after leaching, was removed from the filters, and its pH value was determined by the quinhydrone electrometric method. The pH value was also determined on samples removed from the cultures at the same time but not leached with water.

The pH values of the soil from cultures of each soil moisture content, determined on different dates, were averaged.

Ammonia and nitrate determinations were also made on the cultures during the period of incubation. The intervals of determining the ammonia, nitrates, and pH before leaching are indicated on the time axis of the three dimensional graphs of figures 1, 2, and 3. The averaged results are plotted in figure 13. The curves in figure 13 for the cultures treated with 1 gm. of urea, with the exception of the curve for the pH after the soil had been leached, represent a mean of the surface lines in figures 1, 2, and 3 for given times.

The correlation represented in figure 13 is most easily explained by assuming certain physico-chemical relationships between the colloidal material and soluble salts of the soil. The precise mechanism of this relationship has been the subject of much controversy largely devoted to attempts to demonstrate the chemical or physical nature of the reactions. However, the phenomenon is probably a case of base exchange. Hissink (8), Gedroix (6), Wiegner (20), Kelly and Brown (10), and others have shown that the exchange of cations between soils and salt solutions takes place with great rapidity. The exchangeable ions are regarded as resulting from the ionization of the surface molecules of the colloidal or soil complexes. The surface of the soil complex is considered as forming a double layer probably comparable to the Helmholtz double layer with the cations loosely held in the outer layer of the liquid phase. It has also been observed that certain cations are more strongly held than others, depending on their chemical nature.

The absorbing complex may be assumed to be represented by the following symbol:

| Ca | Na | H | K |
|---|---|---|---|
| Ca | | | $NH_4$ |
| Ca | | | Mg |
| Ca | | | Mg |
| Ca | | | Mg |
| Ca | Soil Complex | | Mg |
| Ca | | | Mg |
| Ca | | | Ca |
| Ca | | | Ca |
| Ca | | | Ca |
| Ca | Ca | Ca | Ca |

The foregoing symbol represents approximately the proportion of replaceable Ca, Mg, Na, and K as determined by Barnette and Hester (1) in a similar soil to that used in this experiment, with regard to soil type and pH value.

However, the proportion of the different cations absorbed by the soil complex has been observed to be dependent on the chemical composition of the soil colloids, the acidity relationship of the soil, and the chemical properties of the cations.

The reactions which urea undergo as the result of the biological activity and the physico-chemical equilibria of the resulting products with the soil are represented as follows:

1. $CO(NH_2)_2 + 2\ H_2O \xrightarrow{\text{urease}} (NH_4)_2CO_3$

2.

| Ca | Na | H | K | | Ca | Na | H | K | |
|---|---|---|---|---|---|---|---|---|---|
| Ca | | | $NH_4$ | | $NH_4$ | | | Mg | $x\ (NH_4)CO_3$ |
| Ca | | | Mg | | Ca | | | $NH_4$ | |
| Ca | | | Mg | | $NH_4$ | | | $NH_4$ | $x\ CaCO_3$ |
| Ca | | | Mg | | Ca | | | Mg | |
| Ca | Soil Complex | | Mg | $+ (NH_4)_2CO_3 \rightarrow$ | $NH_4$ | Soil Complex | | $NH_4$ | $+\ x\ MgCO_3$ |
| Ca | | | Mg | | Ca | | | Mg | |
| Ca | | | Ca | | $NH_4$ | | | $NH_4$ | $x\ K_2CO_3$ |
| Ca | | | Ca | | Ca | | | Ca | |
| Ca | | | Ca | | $NH_4$ | | | $NH_4$ | $x\ Na_2CO_3$ |
| Ca | Ca | Ca | Ca | | $NH_4$ | Ca | $NH_4$ | Ca | |

Alkaline Condition

3. Process of nitrification

(a) $2\ NH_3 + 3\ O_2 \xrightarrow{\text{Nitrosomonas}} 2\ HNO_2 + 2\ H_2O$

(b) $2\ HNO_2 + O_2 \xrightarrow{\text{Nitrobacter}} 2\ HNO_3$

4.

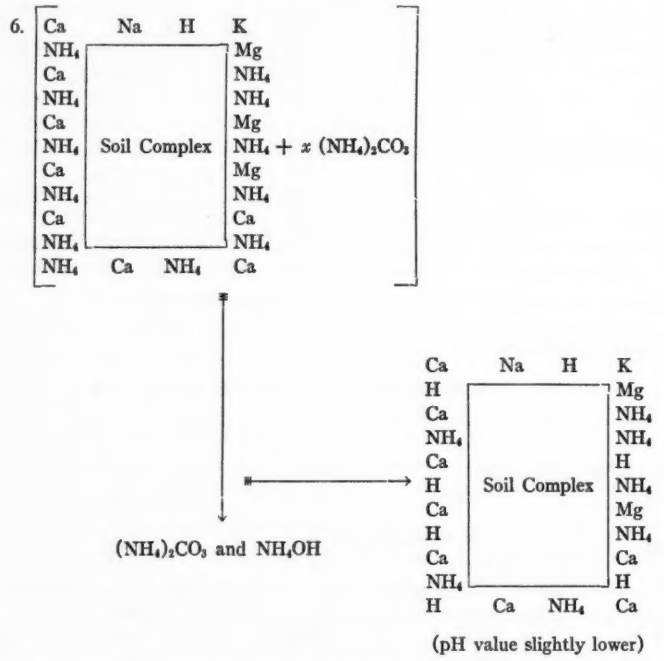
| Ca | Na | H | K | | Ca | Na | N | Mg | |
|---|---|---|---|---|---|---|---|---|---|
| $NH_4$ | | | $NH_4$ | | Ca | | | Mg | |
| Ca | | | Mg | | Ca | | | Ca | |
| $NH_4$ | | | $NH_4$ | (Nitrification) | $NH_4$ | | | Mg | |
| Ca | | | Mg | | Ca | | | $NH_4$ | |
| $NH_4$ | Soil Complex | | $NH_4 + x\ O_2$ | $\longrightarrow$ | Ca | Soil Complex | | Ca | $+\ X\ HNO_3 \times H_2O$ |
| Ca | | | Ca | | Ca | | | Mg | |
| $NH_4$ | | | $NH_4$ | | $NH_4$ | | | Ca | |
| Ca | | | Ca | | Ca | | | Ca | |
| $NH_4$ | | | $NH_4$ | | Ca | | | $NH_4$ | |
| $NH_4$ | Ca | $NH_4$ | Ca | | $NH_4$ | Ca | Ca | Ca | |

5.

| Ca | Na | H | Mg | | Ca | Mg | H | Mg | |
|---|---|---|---|---|---|---|---|---|---|
| Ca | | | Mg | | H | | | H | |
| Ca | | | Ca | | Ca | | | Ca | $x\ KNO_3$ |
| $NH_4$ | | | Mg | | $NH_4$ | | | H | |
| Ca | | | $NH_4$ | | H | | | $NH_4$ | $x\ Ca(NO_3)_2$ |
| Ca | Soil Complex | | Ca | $+ x\ HNO_3 \longrightarrow$ | Ca | Soil Complex | | Ca | + |
| Ca | | | Mg | | H | | | Mg | $x\ Mg(NO_3)_2$ |
| $NH_4$ | | | Ca | | $NH_4$ | | | Ca | |
| Ca | | | Ca | | H | | | H | $x\ NaNO_3$ |
| Ca | | | $NH_4$ | | Ca | | | H | |
| $NH_4$ | Ca | Ca | Ca | | $NH_4$ | Ca | $NH_4$ | Ca | $x\ NH_4NO_3$ |

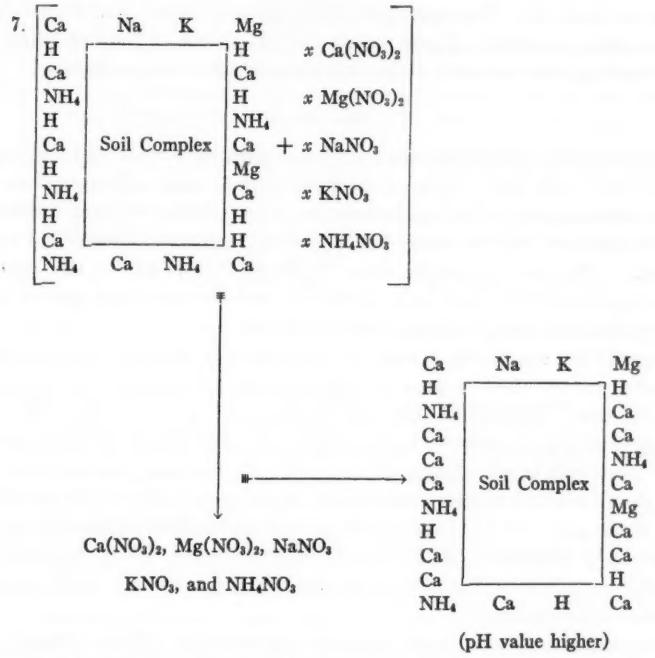
Equations 2, 4, and 5 are assumed to represent in a general way the physico-chemical equilibria between the soil colloids and the chemical compounds present in the soil at different stages of biological activity in the decomposition of urea.

Equation 6 represents a possible explanation for the lowering of the pH value of the soil of low moisture content, where the ammonia content is high and the soluble nitrate content is low. Equation 2 represents the soil complex equilibrium before leaching, and 6 after leaching with water.




The indications are that the removal of some of the ammonia, probably as ammonium carbonate and ammonium hydroxide, from the soil of high ammonia concentration and low nitrate content decreased the pH value of the resultant soil complex in water.

The portion of figure 13 where the pH value of the soil is increased considerably as the result of leaching, is represented by equation 7. Equation 5 represents a similar condition of the soil before leaching.




It is well known among soil workers that the addition of a neutral salt to a suspension of an acid soil liberates a considerable amount of acid, which can be estimated by titration of the filtrate as in the "lime requirement" method of Hopkins (10).

Crowther (4) has shown that the treatment of soils with salt solutions in the laboratory and subsequent leaching with water causes a considerable increase in the pH value of the soil. This observation is borne out in figure 13 for neutral salts which were not added to the soil but were present as the result of biological changes of urea.

The accumulation of relatively large quantities of soluble salts in the soil, resulting from the oxidation of ammonia to nitrate at favorable moisture contents (ranging from 6.80 to 17.95 per cent moisture), decreased the pH value of the soil. Subsequently, the leaching of these soils and the removal of most of the soluble salts gave an equilibrium of the soil with water which was significantly less acid than that of the soil-water-salt equilibria. At 20.55 per cent moisture the nitrate content indicates small quantities of soluble salts, and consequently the pH value was not changed appreciably as the result of leaching.

Further evidence which bears out this relationship between the quantities of different forms of nitrogen in the soil and the extent to which the pH value of the soil is increased as the result of leaching, is shown by the untreated soil at

the top of figure 13. The quantities of nitrogen as ammonia and nitrate in the soil are fairly constant. Consequently the pH values of the soil before and after leaching show a corresponding difference which is fairly constant.

## SUMMARY

Ammonification and nitrification studies of urea were made by mixing given quantities of urea with 5 kgm. of air-dried Norfolk sand. Observations were made on the influence of soil moisture, time, concentration of urea in the soil, and temperature, on the conversion of urea nitrogen to ammonia and nitrate nitrogen. The acidity relationships produced in the soil as the result of accumulated products from urea, ammonia, and nitrates, were studied under both leached and unleached conditions of the soil.

A correlation was found to exist between the soil moisture content and the rate of transformation of urea to ammonia and subsequently to nitrates in Norfolk sand. Apparently the rate of ammonia accumulation from urea decreased with an increase in the soil moisture in the early period of incubation. Later when nitrification began the quantity of ammonia, accumulated from urea, decreased with an increase in soil moisture up to 13.95 per cent on the dry basis of the soil. At 15.85 and 17.95 per cent moisture the ammonia accumulation again increased. At 20.55 per cent moisture, which represents an anerobic condition of the soil (saturated with water), very little ammonia accumulated from urea.

The ammonia formed from urea was converted to nitrate nitrogen very slowly in comparison with the rate of conversion of urea to ammonia. There was no significant production of nitrate nitrogen at 21°C. until 17 days after urea was added to the soil. The optimum soil moisture for nitrate production in Norfolk sand controlled at 21°C. was found to be 13.95 per cent. No nitrates were formed in the culture of 20.55 per cent moisture, which represents anerobic conditions.

The acidity relationships of the soil were counteracted by the two nitrogen transformation products from urea. Ammonia nitrogen increased the pH value, and nitrate nitrogen decreased the pH value of Norfolk sand in soil cultures.

Doubling the concentration of urea in the soil produced a slightly higher concentration of nitrate nitrogen, but calculations for the percentage of urea nitrogen converted to nitrogen as nitrate showed that the conversion was less efficient at the higher concentration of urea.

Over an average daily temperature range varying between 10°C. and 30°C., the fluctuations in the production of nitrates from urea seemed to vary directly with the temperature. At a constant temperature of 21°C. the rate of production was slow at first but increased gradually throughout the experiment.

Leaching the soluble salts, which were produced in the soil from urea as the result of biological changes, increased the pH value of the soil-water suspension. The degree of the change in pH value as the result of leaching was found to be dependent on the concentration of ammonia and nitrate nitrogen in the soil.

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# BORON REQUIREMENTS OF COTTON

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Among those elements which, in addition to the older list of 10 essential elements, are now considered essential to the growth of many if not all plants, boron has received a fairly generous share of attention. In demonstrating the essential nature of this widely distributed element, emphasis has been placed upon the use of specially purified chemicals and upon the use of culture vessels free of boron. The requirements of some plants have been shown to be satisfied when boron is available in the nutrient solution in concentrations considerably below 1 p.p.m. The boron requirements of cereals, if boron is actually essential to their growth, is much lower. The requirements of certain other plants, however, are not satisfied by what may be called traces of boron and, as is shown in table 1, maximum growth and fruitfulness of cotton occur only when this element is supplied in concentrations of 10 p.p.m. in the nutrient solution. An optimum concentration of this magnitude and the concentrations found in the resulting plant material suggest that boron plays a major rôle in cotton metabolism. It has been found that the boron requirement of cotton is among the highest of some 60 plants which have been compared.

In addition to its essential character, boron, when present in excessive concentrations, is highly toxic. This fact has been known for a long time, but only more recently has it been shown that its excessive occurrence (0.5 p.p.m. and upward[2]) in the irrigation waters in a number of areas in arid regions is the cause of certain abnormal symptoms and depressed growth which previously were attributed to other factors. For the past several years the occurrence and effects of boron in irrigation water have been the object of investigations by the U. S. Department of Agriculture, through the Division of Western Irrigation Agriculture. These investigations have disclosed marked differences in the tolerance of different plants to boron and, incidental to the investigations, a wide variability in the requirements of different plants. A number of crop plants have responded favorably to boron concentrations sufficiently high to produce injury or inhibit the growth of boron-sensitive plants. The spread between the suboptimum and excessive concentrations

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[2] The boron concentrations in soil solutions normally exceed those of the irrigation water after prolonged use. Only the more sensitive plants are injured by boron concentrations in irrigation waters as low as 0.5 p.p.m.

for some plants has been found to be so narrow that an actual overlapping of beneficial and injurious effects is indicated. Boron accumulates in leaves with age, and strikingly different concentrations exist in the different plant organs and in different portions of the same organs.

The data on boron relations of cotton as here presented are selected from information being obtained with respect to a number of crop plants in an investigation of the boron problem under western irrigation conditions. The completion of these investigations is not immediately in sight and for that reason it has seemed desirable to call attention to the response of cotton to boron in order that the information might be available in other investigational fields. Much of the earlier work on boron in relation to plant growth has been

TABLE 1

*Effect of boron on growth and yield of acala cotton plants*

| CONCENTRATION OF BORON IN CULTURE SOLUTIONS—*p.p.m.* | "0" | 1 | 5 | 10 | 15 | 25 |
|---|---|---|---|---|---|---|
| *1929* | | | | | | |
| Mean weight of 4 plants.....*gm.* | 114 | ..... | 149 | 177 | 154 | 83 |
| Green bolls on 4 plants, December 9..... | 27 | ..... | 8 | 3 | 6 | 8 |
| Open bolls on 4 plants, December 9..... | 1 | ..... | 22 | 30 | 25 | 11 |
| Weight seed cotton in open bolls.....*gm.* | 5 | ..... | 170 | 241 | 201 | 88 |
| Boron—entire plants,*.....*p.p.m.* | 12 | ..... | 123 | 312 | 361 | 536 |
| Boron per plant,*.....*mgm.* | 1.4 | ..... | 13.1 | 36.4 | 37.3 | 32.8 |
| *1930* | | | | | | |
| Mean weight of 4 plants.....*gm.* | 51 | 124 | 150 | 195 | 110 | 133 |
| Green bolls on 4 plants, November 14..... | 3 | 17 | 25 | 34 | 21 | 17 |
| Open bolls on 4 plants, November 14..... | 0 | 5 | 3 | 3 | 2 | 4 |
| Boron—leaves only.....*p.p.m.* | 16 | 187 | 306 | 522 | 833 | 1,625 |
| Boron—stems and roots only.....*p.p.m.* | 15 | 24 | 32 | 33 | 48 | 60 |
| Boron per plant†.....*mgm.* | 0.7 | 6.4 | 12.4 | 26.4 | 25.4 | 53.6 |

* Seed cotton not included.

† Burs and seed cotton not included.

of a qualitative, or exploratory, character, in that only a few investigators have undertaken accurate boron determinations to observe either the rate of absorption of boron from nutrient solutions or the extent to which the toxic or beneficial effects of boron are associated with its accumulation and distribution in the plant.[3]

The experimental plants discussed were grown in large sand beds[4] so equipped with plumbing, supply barrels, and drains that the nutrient solution held by the sand could be reestablished each day by flooding and draining to maintain the concentration of boron and at the same time provide like conditions for the different plants undergoing comparison in each bed.

[3] Acknowledgment is made to Mr. L. V. Wilcox for the boron determinations herein reported.

[4] F. M. EATON. 1931 A large sand culture apparatus. *Soil Sci.* 33: 235–240.

In 1929 five boron concentrations were employed; namely, "0", 5, 10, 15, and 25 p.p.m., and in 1930 a 1 p.p.m. concentration in addition. The concentrations are in terms of elemental boron supplied as boric acid. The nutrient solutions contained (in addition to boron, iron, and manganese) calcium nitrate, magnesium sulfate, and potassium acid phosphate in concentrations of 6, 3, and 3 millimoles per liter respectively. As a result of impurities of the "C. P." chemicals employed and of the free exposure of the beds out of doors, the "0" bed solution contained approximately 0.05 p.p.m. of boron.

Each of the more important crops compared has been grown during at least two seasons to compensate in part for the necessarily limited number of plants involved.

Table 1 compares the growth and fruitfulness of Acala upland cotton grown in the different beds during each of two seasons. In both years the plants in the "0" bed shed most of their floral buds and bolls. Only one undersized open boll was produced in this bed in 1929, and in 1930 no bolls set previous to October were retained. The plants of the "0" bed were shorter than those of the 1 or 5 p.p.m. beds and the branch lengths were reduced. The leaves of the "0" bed cotton were characterized by mildly arrested development of the veins resulting in some buckling of the mesophyll, by marked irregularities in shape, and by large irregular areas which died out after having become chlorotic.

No deficiency symptoms could be noted in the plants supplied with 1 p.p.m. of boron and except for their smaller size and lighter crop, as compared with higher concentrations, they would have been considered normal.

The largest plants and the greatest number of bolls resulted in each season in the culture bed supplied with nutrient solution containing 10 p.p.m. of boron. The plants of the 10 p.p.m. bed, producing as they did the highest yield, showed very mild but definite burning of the leaves, both marginal and in intravenous spots adjacent to the margins. This type of burning, commonly preceded by yellowing, which is characteristic of boron injury, did not occur in the 5 p.p.m. concentration. The concentration of boron, other than in the "0" bed, did not influence the weight of individual bolls or the seed cotton per boll.

As shown in table 1, 1930, the boron concentrations in the leaves greatly exceeded that of the stems and roots, and these concentrations increase as the boron supplied is increased.

The burs were not included in the analyses of the 1930 plants but in 1929, when boron determinations were made on entire plants, exclusive of seed cotton, the cotton of the 10 p.p.m. bed accumulated 36.4 mgm. of boron per plant. An acre of 14,000 such plants under similar conditions would have removed from the soil 510 gm. of boron, or 5.2 pounds of anhydrous sodium borate, or 9.9 pounds of 10 hydrate borax ($Na_2B_4O_7 \cdot 10H_2O$).

When borax is applied to a soil only a portion of it remains dissolved in

the soil solution. If the soil to which it is added is low in boron a very considerable part of it may be rendered unfree, or insoluble, by the soil. In contrast with nitrates, which are readily removed from soil by one or two leachings, a number of successive percolates or extractions are required to recover a major part of boron similarly added. The extent to which boron is rendered partially insoluble by different soils varies greatly. For these reasons it cannot be stated in advance how much boron would have to be added to a particular soil to produce a soil solution of any desired concentration.

During and following the War considerable injury resulted when potash salts containing boron were used as fertilizers in the cotton belt and elsewhere. This injury was the cause of serious concern on the part of farmers and was made the subject of investigations, both by a number of the state experiment stations and by the U. S. Department of Agriculture.[5] These reports show that the higher concentrations used caused serious injury, but for cotton the effects of the smaller applications were uncertain. Heavy rains following the applications served to lessen the injury. Two features of these investigations are of primary interest here: (*a*) The borax in those tests was either placed directly in the drill rows or was broadcast above the drill rows at or near the time of planting, and (*b*) adequate studies are not reported of the residual effects of the boron on yields during succeeding years. An element as toxic as boron would be expected to produce highly injurious effects when concentrated in a restricted portion of the root zone and it is surprising that applications of 10 pounds of anhydrous borax to the acre made in this way did not produce injurious effects in all of the tests.

Indirect evidence tending to support the view that applications of boron under field conditions may have a beneficial effect upon cotton is found in the results of nitrate fertilizer trials at the Delta Experiment Station of Mississippi. The Delta Station Service Sheets No's. 23 and 29 show that the continued use of Chilean sodium nitrate has resulted in higher yields than those resulting from synthetic nitrate fertilizers. Five-year averages show an increased yield of the sodium nitrate plats over calcium nitrate plats of 172 pounds of seed cotton to the acre and nine-year averages show sodium nitrate to have increased the yield by 32 pounds over ammonium nitrate. Of the latter it is stated in footnote that for the years 1926–27–28–29 the average increase for sodium nitrate was 788 pounds an acre, for ammonium sulfate 498 pounds, and for cyanamid 528 pounds. Analyses made by this laboratory have shown two samples of Chilean sodium nitrate to have contained respectively 298 and 176 p.p.m. of boron and the producers report an analysis showing 791 p.p.m. of boron. It is probably natural that variability should be shown in the impurities in a product of this character. A sample of a newer, more refined, form of Chilean sodium nitrate, the Champion Brand, contained by our analysis 76 p.p.m. of boron and the latter of the Service Sheets cited indicates a

[5] SKINNER, J. J., BROWN, B. E., AND REID. F. R. 1923 Effect of borax on the growth and yield of crops. U. S. Dept. Agr. Dept. Bul. 1126.

slightly lower yield when it is used as a fertilizer. Each of the few determinations on synthetic nitrate fertilizers made by us have shown these products to be essentially free of boron. Although relatively small additions of boron to boron deficient soils might produce outstanding effects, this explanation of an apparent advantage resulting from the boron carried by nitrate of soda is nevertheless inconclusive, since annual applications of 200 pounds of material carrying 790 p.p.m. of boron would add to the soil but 72 gm. of boron a year.

The experimental evidence here presented is believed to indicate that gratifying results might follow the use of boron as a fertilizer in cotton field tests. In those localities where increased yields might result, the optimum concentrations would doubtless be relative to the physical characteristics of different soils and their initial boron concentrations. It is believed that boron used as a fertilizer should be incorporated in the soil well in advance of planting and it is possible that boron in a form more slowly soluble than borax, such as colemanite ($2CaO \cdot B_2O_3,5H_2O$) might be most desirable. Some of the winter crops, such as Melilotus, Winsor beans, and vetch, are highly tolerant to boron, as are alfalfa and beets. Boron should not be applied immediately before corn, other cereals, or beans, since a growth depression of 25 per cent or more can be expected at soil solution concentrations optimum for cotton.

# SOLUBLE ALUMINUM STUDIES: II. MINIMUM CONCENTRATIONS OF ALUMINUM FOUND TO BE TOXIC TO CORN, SORGHUM, AND BARLEY IN CULTURE SOLUTIONS[1, 2]

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It has been shown in some previous work reported from this laboratory (17), as well as in some earlier work by Magistad (11) and by Pierre (16), that the concentrations of soluble aluminum in the displaced solution of acid field soils are comparatively low. Therefore, in determining the validity of the toxic aluminum theory of soil acidity, a question of prime importance is: are these relatively low concentrations of soluble aluminum found in acid soils sufficiently high to be injurious to the growth of plants?

The general problem of determining the concentrations of aluminum required to be toxic to plant growth has been studied quite extensively by means of culture solutions (2, 3, 8, 9, 10, 18, 20). The results obtained, however, are very conflicting and in most cases their interpretation is difficult. This is mainly because of the failure of many investigators to recognize the various factors which affect the solubility of aluminum and also the secondary effects of additions of aluminum salts to culture solutions. Line (7) and Gile (5) have discussed some of these factors in considerable detail and have questioned many of the experiments upon which the toxic aluminum theory of soil acidity is based.

Among the main criticisms of the culture-solution investigations on aluminum toxicity may be listed the following:

Failure to maintain constant the H-ion concentration of the culture solutions.

Failure to maintain the desired aluminum concentrations or to make determinations of the concentration of aluminum found in solution.

Failure to consider the mutual precipitating action of aluminum and phosphate in the culture solution.

Growing the plants in very small culture vessels and harvesting the plants at too early a stage of growth.

It is noteworthy that in none of the experiments which have been reported were determinations made of the concentration of aluminum actually present in the culture solution during the growth of the plants. This no doubt is due partly to the fact that until recently there was no accurate method for determining small amounts of aluminum. The solubility of aluminum is primarily a function of the hydrogen-ion concentration. It is well known, however, that plants may rapidly alter the pH of the culture solutions. This is especially true if the culture vessels are small. Since a rise in pH readily causes precipitation of aluminum, it is evident that the pH values of the cultures should be accurately controlled. Moreover, since it has been shown that aluminum phosphate is precipitated even at low pH values, the addition of aluminum salts to complete nutrient solutions may cause the precipitation of aluminum as well as of phosphate. Thus it is possible that in such cases the poor plant growth which results may be due to phosphate starvation rather than to aluminum toxicity.

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[2] Contribution from the Department of Agronomy and Genetics.

McLean and Gilbert (9, 10) in their experiments recognized the precipitating action of aluminum on phosphate and prevented this from taking place by alternating their plants between complete nutrient solutions containing phosphate and complete nutrient solutions minus phosphate but containing aluminum. For this reason their results are probably the most satisfactory that have been reported regarding the minimum concentrations of aluminum found toxic to the growth of plants. Their minimum toxic concentrations, however, were in many cases considerably higher than the concentrations ordinarily found in the displaced solution of acid field soils, as will be discussed more fully later. Magistad (11) in a comprehensive investigation grew a number of different plants in sand cultures to which was added Hartwell and Pember's nutrient solution, with and without aluminum, adjusted to different pH values. Since the culture vessels were small, it was difficult to maintain the reactions of the culture solutions closer than to within 0.4 to 1.0 pH unit even though they were adjusted twice daily. Moreover, iron phosphate was mixed with the sand to furnish additional phosphorus; and, since no determinations were made of the amount of aluminum remaining in solution, it is not possible to be sure of the concentrations of aluminum present in the cultures. The results obtained, however, indicate that relatively low concentrations of aluminum may be toxic to plant growth.

In many of the other investigations where aluminum was found toxic to plants in culture solutions (1, 3, 4, 6, 12, 18) the experiments were planned primarily to prove the toxicity of aluminum rather than to determine very accurately the minimum concentrations required to cause injury. These and other investigations previously mentioned will not be discussed here because they are difficult to interpret accurately and because Line, Magistad, and others have already made critical reviews.

The objectives of the present investigation were: first, to study the relative effect of hydrogen-ion concentration and aluminum concentration on plant growth; and second, to determine the minimum concentrations of aluminum found injurious to three crop plants which have been reported as showing different degrees of tolerance to soluble aluminum.

## METHODS OF PROCEDURE

The three kinds of plants used in this study were barley, sorghum, and corn. These plants are classified by McLean and Gilbert (9) as being sensitive, medium sensitive, and resistant to soluble aluminum, respectively. Since Hartwell and Pember's nutrient solution (6) has been extensively used in aluminum studies by other investigators and since it has the advantage of resembling the soil solution in phosphate concentration more than do most nutrient solutions, it was used in this investigation with slight modifications. The modifications consisted in omitting the ferric nitrate, in adding 0.25 p.p.m. of boric acid and 0.38 p.p.m. of manganese sulfate, and in substituting mono-potassium phosphate for mono-calcium phosphate in equivalent amounts. In order to prevent precipitation of the aluminum as aluminum phosphate, a method was used similar to that of McLean and Gilbert (9, 10) of alternating the plants between complete nutrient solutions and similar solutions containing no phosphorus but containing aluminum. The plants were changed from one of these series to the other each day instead of twice a week, as was done by these investigators. Once a week, or oftener, if the plants appeared to need iron, they were put in a third series of pots containing Hartwell and

Pember's nutrient solution minus the phosphate but containing 2.77 p.p.m. of iron as the tartrate and kept at pH 4.5. Distilled water was used except for the iron series of cultures, where tap water was employed. New culture solutions were made up about every three weeks during the progress of the experiment.

Six different treatments were studied, and the cultures were in triplicate. In order to keep the aluminum in solution, the pH values of all the cultures, except those of treatment 1, were kept at 4.5. The cultures of treatment 1 were kept at pH 6.0 as a control on the effect of hydrogen-ion concentration on the growth of the plants. Treatments 2 to 6 inclusive, received 0, 1, 2, 5, and 10 p.p.m. of aluminum, respectively. Determinations of the pH value of the solutions were made daily, and the solutions were adjusted, if necessary, by additions of sodium hydroxide. Phosphate and aluminum determinations were made at frequent intervals, and additional amounts of potassium phosphate were added when found necessary to maintain the original concentration of phosphate. Aluminum was determined by a slight modification of the "aluminon" method (17), and phosphorus was determined by the blue colorimetric method (14).

The culture vessels were glazed earthenware pots of approximately 15-liter capacity. They were covered with galvanized lids containing three holes of such size as to hold paraffined corks 2.5 inches in diameter. Each cork contained three holes in which the plants were held upright by means of nonabsorbent cotton.

The corn, barley, and sorghum were germinated in clean quartz sand, and the corn seedlings were transferred to the culture solutions on August 30; the barley seedings, on September 3; and the sorghum seedlings, on September 8. The three crops were grown together during the first part of the experiment, each culture vessel receiving three seedlings of each plant. Later the number of seedlings in each cork was reduced to two. When the corn plants grew large enough to shade the barley and sorghum, they were removed to separate culture vessels, and each plant was placed in a separate cork. Later, when the barley and sorghum plants appeared too crowded, they were also placed in separate culture vessels.

Notes of the plants were taken as differences became apparent, and just prior to harvesting, photographs of the crops were taken. The corn plants were harvested on October 10, and the barley and sorghum plants were cut on December 6.

## RESULTS OF INVESTIGATION

### *Control of nutrient solutions*

The procedure which has just been described made possible an accurate control of the phosphorus, aluminum, and hydrogen-ion concentration of the culture solutions. This is shown for aluminum and hydrogen-ion concentra-

tion in table 1. The pH values of the solutions kept at pH 4.5 were found to decrease only very slightly during a 24-hour period, the maximum daily change being in most cases less than one-tenth of a pH unit. The various concentrations of aluminum in the culture solutions were also well maintained except where 10 p.p.m. of aluminum had been added. It will be noted that during the period between September 8 and October 3, the average amounts of aluminum found in solution in cultures 6A, 6B, and 6C were less than in cultures 5A, 5B, and 5C, where only half as much aluminum had been added. This was found to be due to some silica in the sodium hydroxide used to adjust the reaction of the culture solutions. Aluminum silicate is precipitated even at relatively low pH values and since more alkali was necessary to correct the acidity formed when the largest amount of aluminum was added, less alumi-

TABLE 1

*Treatment of cultures and analyses of solutions with respect to aluminum and hydrogen-ion concentration during various periods of plant growth*

| CULTURE NO. | TREATMENTS | | ANALYSES OF CULTURE SOLUTIONS* | | | |
|---|---|---|---|---|---|---|
| | | | Sept. 8–Oct. 3 | | Oct. 16–Nov. 14 | |
| | Aluminum | H-ion concentration | H-ion concentration | Aluminum | H-ion concentration | Aluminum |
| | *p.p.m.* | *pH* | *pH* | *p.p.m.* | *pH* | *p.p.m.* |
| 1. A, B, C | None | 6.0 | 5.69 | 0 | 5.79 | 0 |
| 2. A, B, C | None | 4.5 | 4.38 | 0.03 | 4.47 | 0.02 |
| 3. A, B, C | 1.0 | 4.5 | 4.41 | 1.03 | 4.46 | 1.07 |
| 4. A, B, C | 2.0 | 4.5 | 4.36 | 2.28 | 4.41 | 2.47 |
| 5. A, B, C | 5.0 | 4.5 | 4.39 | 4.56 | 4.44 | 4.64 |
| 6. A, B, C | 10.0 | 4.5 | 4.40 | 4.06 | 4.42 | 7.55 |

* The values given are averages of daily determinations in the case of pH values; the averages for the aluminum concentration are for five sets of determinations during the first period and three sets of determinations during the second period.

num remained in solution with the addition of 10 p.p.m. than with the addition of 5 p.p.m. During the latter part of the investigation the aluminum chloride solution used was prepared from the salt rather than from pure aluminum metal dissolved in strong hydrochloric acid. It was, therefore, less acid and since less sodium hydroxide was required to neutralize the acidity, less aluminum was precipitated as the silicate.

The phosphate concentration of the nutrient solutions remained near the original concentration during the earlier periods of growth. As the plants became older and absorbed more phosphorus, the concentraton in the culture solutions was rapidly lowered. This is especially true in cultures 1 and 2, where the growth was best. In no case, however, did the phosphate concentration ever become lower than 0.5 p.p.m., a concentration found by Parker (13) to be sufficiently high for the maximum growth of corn.

*Effect of soluble aluminum on plant growth*

The injurious action of aluminum on the growth of the plants became evident at a very early stage of growth. With corn, which grew vigorously from the time it was placed in the nutrient solutions, injury was apparent in the roots after the third day in the aluminum solution, even where only 1 p.p.m. of aluminum was present. This injury was evidenced by a tendency toward stubbiness and a decrease in the number of lateral roots. The damage increased with increasing concentrations of aluminum. Soon the roots of the plants which were grown in solution cultures receiving aluminum became brownish in color, particularly the tips of the roots. The effects of aluminum on the tops were much slower in developing, becoming apparent only after the second week of growth. This injury was more evident in the size of the stalk than in the height of the plants and was more pronounced with increasing concentrations of aluminum.

The injuries to barley and sorghum were also evident at an early stage of growth with 1 p.p.m. of aluminum. As in the case of corn, the damage to the roots preceded decreased growth of tops, and the extent of injury increased with increasing concentrations of aluminum and with the age of the plants. The characteristic effects on sorghum are well shown in plate 1, figure 2. It will be noted that the injury from 1 p.p.m. of aluminum in culture 3C is very evident in both tops and roots. The leaves show a characteristic chlorosis similar to type-B chlorosis of corn described by Pettinger et al. (15). The roots, however, have the most pronounced lesions. They show very well the characteristic stubbiness, the absence of lateral roots, and the pronounced browning of the root tissue. In general, these characteristics agree with the descriptions given by other investigators (6, 8, 9, 11).

The corn plants were cut on October 10, whereas the barley and sorghum plants were cut on December 6. The appearance of the plants at harvest time is shown in plates 1 and 2; the yields of roots and tops are given in tables 2, 3, and 4.

It will first be noted from table 2 that the weight of corn in culture solutions without aluminum was only about one-half as much when grown at pH 4.5 as when grown at pH 6.0. The presence of 1 p.p.m. of aluminum in culture solutions of pH 4.5 reduced the yields about 25 per cent, whereas the presence of 2.28 and 4.56 p.p.m. reduced the yields 39 and 59 per cent respectively.

The yields of the sorghum plants at harvest time are given in table 3. It will be noted that the total yields in cultures without aluminum was about 70 per cent as high at pH 4.5 as at pH 6.0. When the nutrient solutions contained 1.04, 2.34, and 4.63 p.p.m. of aluminum, the yields at pH 4.5 were reduced 16, 82, and 87 per cent, respectively. The top-root ratio values, given in the last column of table 3, substantiate the conclusions obtained from observations on the appearance of the plants, namely, that the roots are relatively more injured than the tops by the presence of aluminum.

TABLE 2

*Average yields of corn in culture solutions of different aluminum and hydrogen-ion concentrations*

(Average weights of two plants)

| CULTURE NO. | pH OF SOLUTION | ALUMINUM | | TOPS | | | ROOTS (OVEN-DRY) | TOTAL WEIGHT | | TOP / ROOT |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Added | Average amount in solution | Green weight | Oven-dry weight | Per cent dry matter | | Absolute | Relative | |
| | | *p.p.m.* | *p.p.m.* | *gm.* | *gm.* | | *gm.* | *gm.* | | |
| 1. A, B, C | 6.0 | 0 | 0 | 304.1 | 42.7 | 14.4 | 5.5 | 48.2 | 198 | 7.8 |
| 2. A, B, C | 4.5 | 0 | 0.03 | 203.9 | 20.7 | 10.1 | 3.6 | 24.3 | 100 | 5.8 |
| 3. A, B, C | 4.5 | 1.0 | 1.03 | 148.9 | 16.2 | 10.9 | 2.2 | 18.4 | 75 | 7.4 |
| 4. A, B, C | 4.5 | 2.0 | 2.28 | 124.1 | 12.6 | 10.1 | 2.1 | 14.7 | 61 | 6.0 |
| 5. A, B, C | 4.5 | 5.0 | 4.56 | 87.5 | 8.6 | 9.8 | 1.3 | 9.9 | 41 | 6.6 |
| 6. A, B, C | 4.5 | 10.0 | 4.06 | 93.9 | 9.4 | 10.0 | 1.4 | 10.8 | 45 | 6.7 |

TABLE 3

*Average yields of sorghum in culture solutions of different aluminum and hydrogen-ion concentrations*

(Average weights of two plants)

| POT NO. | pH OF SOLUTION | ALUMINUM | | TOPS (OVEN-DRY) | ROOTS (OVEN-DRY) | TOTAL WEIGHT | | TOP / ROOT |
|---|---|---|---|---|---|---|---|---|
| | | Added | Average amount in solution | | | Absolute | Relative | |
| | | *p.p.m.* | *p.p.m.* | *gm.* | *gm.* | *gm.* | | |
| 1. A, B, C | 6.0 | 0 | 0 | 10.43 | 2.22 | 12.65 | 146 | 4.7 |
| 2. A, B, C | 4.5 | 0 | 0.02 | 6.97 | 1.70 | 8.67 | 100 | 4.1 |
| 3. A, B, C | 4.5 | 1.0 | 1.04 | 6.07 | 1.25 | 7.32 | 84 | 4.9 |
| 4. A, B, C | 4.5 | 2.0 | 2.34 | 1.42 | 0.18 | 1.60 | 18 | 7.9 |
| 5. A, B, C | 4.5 | 5.0 | 4.63 | 1.02 | 0.13 | 1.15 | 13 | 7.8 |
| 6. A, B, C | 4.5 | 10.0 | 5.41 | 0.72 | 0.08 | 0.80 | 9 | 9.0 |

TABLE 4

*Average yields of barley in culture solutions of different aluminum and hydrogen-ion concentrations*

(Average weights of two plants)

| POT NO. | pH OF SOLUTION | ALUMINUM | | TOPS (OVEN-DRY) | ROOTS (OVEN-DRY) | TOTAL WEIGHT | | TOP / ROOT |
|---|---|---|---|---|---|---|---|---|
| | | Added | Average in solution | | | Absolute | Relative | |
| | | *p.p.m.* | *p.p.m.* | *gm.* | *gm.* | *gm.* | | |
| 1. A, B, C | 6.0 | 0 | 0 | 15.92 | 1.53 | 17.45 | 105 | 9.6 |
| 2. A, B, C | 4.5 | 0 | 0.02 | 15.23 | 1.40 | 16.63 | 100 | 9.2 |
| 3. A, B, C | 4.5 | 1.0 | 1.04 | 6.15 | 0.45 | 6.60 | 40 | 13.6 |
| 4. A, B, C | 4.5 | 2.0 | 2.34 | 4.18 | 0.38 | 4.56 | 26 | 11.0 |
| 5. A, B, C | 4.5 | 5.0 | 4.63 | 4.27 | 0.37 | 4.64 | 28 | 11.6 |
| 6. A, B, C | 4.5 | 10.0 | 5.41 | 2.32 | 0.22 | 2.54 | 15 | 10.5 |

Table 4 and plate 2 show the results obtained with barley. It will be noted that in contrast to the results obtained with corn and sorghum, an increase in the hydrogen-ion concentration from pH 6.0 to 4.5 has reduced the yield of barley only very slightly. The presence of small amounts of aluminum, however, has had a marked deleterious effect. One part per million of aluminum has reduced the yields of tops 60 per cent and of roots 68 per cent, and the total yields in the presence of 2.34, 4.63, and 5.41 p.p.m. of aluminum have been reduced 74, 72, and 85 per cent, respectively. The relatively greater reduction in the yield of roots than of tops from the presence of aluminum has been much greater with barley than with corn, as will be seen from the top-root ratio values given in the last column.

## GENERAL DISCUSSION

The data presented in this study show conclusively that relatively low concentrations of aluminum in culture solutions are toxic to the growth of plants. All three plants studied—corn, sorghum, and barley—were injured by 1 p.p.m. of aluminum in culture solutions at pH 4.5. At this concentration of aluminum, barley showed the greatest reduction in yield; corn, the next greatest; and sorghum, the least. The injury to the roots, however, was much more pronounced with sorghum than with corn, and at higher concentrations of aluminum, sorghum was injured considerably more than was corn. This order of injury is the same as that reported by McLean and Gilbert (9). The concentrations required to be injurious as found in this study, however, are considerably lower than has been reported by these investigations. This is especially true of corn. Thus McLean and Gilbert in their classification of plants as regards injury from aluminum place corn in the resistant group, the plants of which are "depressed by 14 p.p.m. of added aluminum or more." Barley is placed in the sensitive group of plants which are "depressed by 2 p.p.m. of added aluminum," whereas sorghum is considered mediumly sensitive, being "depressed by 7 p.p.m. of added aluminum or less." They give some data on the yield from cultures with and without aluminum which is some cases indicate toxicity at concentrations lower than those given in their classification. In a later investigation, however (10), these same authors found that the addition of 13.6 p.p.m. of aluminum resulted in yields of corn 93 to 96 per cent as high as where no aluminum had been added. They also found that rye, oats, alfalfa, buckwheat, onions, and redtop were stimulated by additions of 3.4 to 13.6 p.p.m. of aluminum in culture solutions. Moreover, the tap water used in these investigations contained 3 to 4 p.p.m. of aluminum. In this same investigation 5 p.p.m. of aluminum added as the citrate to nutrient solutions made with distilled water stimulated the growth of barley while 16 p.p.m. slightly depressed the growth. The addition of 5 p.p.m. of aluminum sulfate to nutrient cultures made up with tap water was slightly injurious to barley when small amounts of phosphate were present but gave no harmful effect with large amounts of phosphate. The addition of 16 p.p.m. aluminum depressed the yields of barley considerably.

The results of the investigations by McLean and Gilbert are reviewed in some detail here because they were conducted in such a way that there was no mutual precipitation of aluminum and phosphate; therefore they are not subject to one of the most serious criticisms of culture solution work with aluminum. Probably the chief criticism of these investigations is that one to six plants were grown in jars of only 250 cc. capacity. As a result, the total growth made by the plants even when no aluminum was added was very small. Moreover, the use of such small culture vessels must have resulted in a rapid change in the pH of the solutions. The pH values of certain cultures after plants had been in them for two days are given. Thus, with nutrient solutions having an original pH value of about 4.5, corn raised the pH value to 6.7; barley, to 6.4; but sorghum decreased the pH value to 3.9. It seems probable, therefore, that in some of the cultures not all of the aluminum added remained in solution. This would tend to explain why the minimum toxic concentrations found by these investigators were considerably higher than those reported in this study.

In a previous investigation by one of the writers (16) and later in a more comprehensive study in this laboratory (17) it was found that the concentrations of aluminum in acid soils were relatively low. As a result of the latter investigation it was concluded that in average field soils at pH 4.5 or above, the displaced soil solution usually contains less than 5 p.p.m. of aluminum, whereas soils of pH 5.0 seldom contain as much as 1 p.p.m. of aluminum in solution. Since it was found that a lowering of the salt concentration of the soil reduced the concentration of soluble aluminum at given pH values, it was concluded that in the presence of a crop or where frequent rains keep the salt content of the soil very low, the concentrations of aluminum in the displaced soil solution may not be more than 1 p.p.m. at pH 4.5, and still less at higher pH values. In view of these considerations and the relatively high concentrations of aluminum which had been found necessary by various investigators to produce toxicity in culture solutions, it was at first believed that the small concentrations of soluble aluminum present in acid soils could not have much effect on the growth of plants. In view of the results obtained in this investigation, however, it is apparent that this conclusion may not be warranted, since a concentration of 1 p.p.m. of aluminum was found injurious to all three crops studied and since it is quite likely that even lower concentrations would have been found injurious if they had been included in the study.

In applying results of culture solutions to soils it must be recognized, of course, that various factors may influence the concentrations of aluminum required to be toxic and, moreover, that these factors may be different under culture solution than under soil conditions. Thus some evidence was obtained by one of the writers (16) that the greater the percentage base saturation of soils the higher the concentration of aluminum required to be toxic. The injury from a given amount of aluminum is also believed by some investigators to be dependent at some extent on the composition of the nutrient solution

(1, 8, 18). Moreover, Spencer (19) in some work with Rhodondendron, which has recently appeared in abstract form, concludes that "in general, the toxic action of aluminum decreases as the acidity of the solution increases."

A significant point that should be emphasized in applying the results of culture solutions to soil is that aluminum causes greater injury to the roots than to the tops of plants. In this investigation, for example, the top growth made by sorghum in the presence of 1 p.p.m. of aluminum was nearly as good as where no aluminum was present. The roots, however, were very badly injured (fig. 2). It appears, therefore, that in spite of their poor growth and severely injured condition, the roots were able to obtain enough nutrients from the solution to make a fair growth of top. Under soil conditions where the nutrients may not be as readily available, it is reasonable to suppose that a poor root system would be less able to absorb the necessary nutrients than in nutrient solutions, and consequently greater injury to the plant would result. This is indicated by the investigations of McLean and Gilbert (9) in which they found that plants injured by aluminum absorb dyes, nitrates, and water less readily than do normal plants.

It may also be expected that the injury from a given concentration of aluminum will be greater under unfavorable conditions of growth in soils than under more favorable conditions. In times of drought, for example, injury to plant growth from soluble aluminum might be greater than under conditions of normal rainfall for two reasons: (a) Low rainfall would mean little leaching and a high salt concentration in the soil and, therefore, a relatively high concentration of aluminum in the soil solution, and (b) plants injured by aluminum would suffer relatively more than normal plants from a lack of moisture, since they would not be able to utilize the moisture present as efficiently.

These considerations emphasize the need of determining the importance of various factors which may influence the concentrations of aluminum required to be toxic to various plants both in culture solutions and in soils.

## SUMMARY

Corn, sorghum, and barley were grown in culture solutions with the purpose of determining the minimum concentration of soluble aluminum required to cause toxicity. The plants were alternated daily between complete nutrient solutions and similar solutions containing aluminum but no phosphate in order to prevent the precipitation of aluminum phosphate. Large culture vessels were used so as to make possible an accurate control of the aluminum, the phosphate, and the hydrogen-ion concentration of the nutrient solutions. The results obtained may be briefly summarized as follows:

Aluminum, present in the culture solutions in concentrations as low as 1 p.p.m., was definitely injurious to the growth of all three plants studied.

Increasing the concentration of aluminum above 1 p.p.m. progressively increased the injury to plant growth.

In the presence of 1 p.p.m. of aluminum, barley was most seriously injured. At higher

concentrations of aluminum, however, sorghum was injured more than barley, and corn was considerably less injured than either barley or sorghum.

The injurious action of aluminum was first noted in the roots and became more evident in both roots and tops with increasing age of the plants.

An increase in the hydrogen-ion concentration of the nutrient solution from pH 6.0 to 4.5 was most injurious to the growth of corn, less injurious to the growth of sorghum, and least injurious to the growth of barley.

These results show that aluminum may be injurious to plant growth in lower concentrations than have generally been considered necessary. It is pointed out that these concentrations of aluminum are within the range found in the displaced solution of acid soils of pH 4.5 to 5.0 and, therefore, that plant growth on such soils may be seriously injured from the presence of soluble aluminum.

Some of the factors which may influence the concentrations of aluminum required to be toxic both in culture solutions and in soils are briefly discussed.

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PLATE 1

EFFECT OF VARIOUS CONCENTRATIONS OF ALUMINUM ON GROWTH OF CORN AND SORGHUM

FIG. 1. Effect on corn.

Culture No. 1—pH 6.0. No. Al
Culture No. 2—pH 4.5. No. Al.
Culture No. 3—pH 4.5. 1.03 p.p.m. Al.
Culture No. 4—pH4.5. 2.88 p.p.m. Al.
Culture No. 5—pH 4.5. 4.56 p.p.m. Al.
Culture No. 6—pH 4.5. 4.06 p.p.m. Al.

FIG. 2. Effect on sorghum.

Culture No. 1C—pH 6.0. No Al.
Culture No. 2C—pH 4.5. No Al.
Culture No. 3C—pH 4.5. 1.04 p.p.m. Al.
Culture No. 4C—pH 4.5. 2.34 p.p.m. Al.
Culture No. 5C—pH 4.5. 4.63 p.p.m. Al.

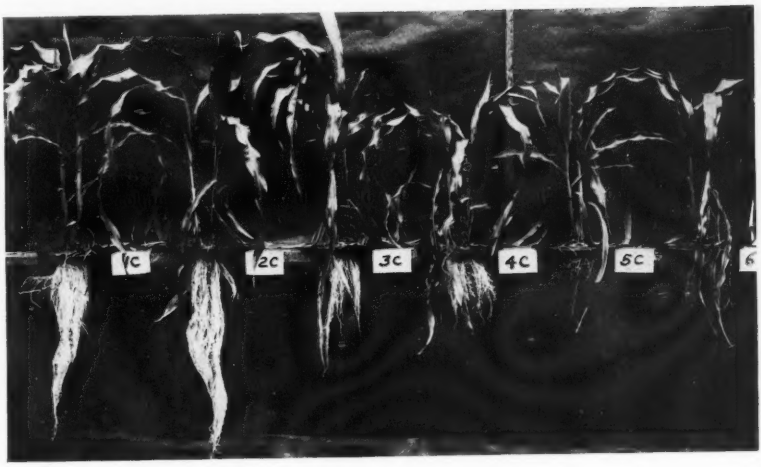



FIG. 1

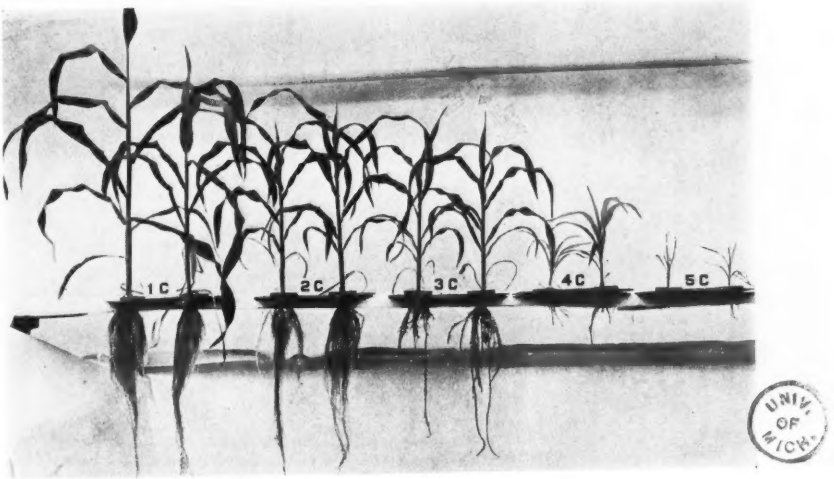
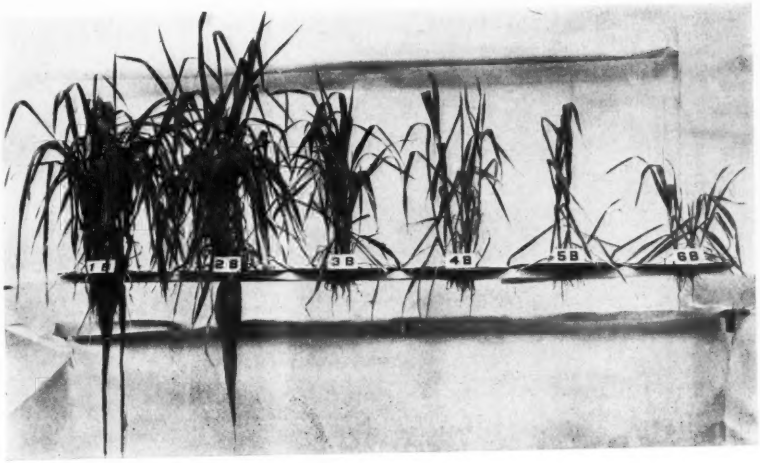



FIG. 2

PLATE 2

EFFECT OF VARIOUS CONCENTRATIONS OF ALUMINUM ON GROWTH OF BARLEY

Culture No. 1—pH 6.0. No. Al.
Culture No. 2—pH 4.5. No Al.
Culture No. 3—pH 4.5. 1.04 p.p.m. Al.
Culture No. 4—pH 4.5. 2.34 p.p.m. Al.
Culture No. 5—pH 4.5. 4.63 p.p.m. Al.
Culture No. 6—pH 4.5. 5.41 p.p.m. Al.

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